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Comparative petrographic, petrochemical and spectrographic analyses of the Precambrian granitic rocks of southeastern Missouri

Eva B. Kisvarsanyi

COMPARATIVE PETROGRAPHIC, PETROCHEMICAL AND SPECTROGRAPHIC ANALYSES OF THE PRECAMBRIAN GRANITIC ROCKS OF SOUTHEASTERN MISSOURI

BY

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A

THESIS

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Approved by

Paul Dean Proctor (advisor) William J. James

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ABSTRACT

Petrographic, petrochemical and spectrographic studies were completed on selected Precambrian granitic rock samples from Southeastern Missouri. This investigation contributes to a more detailed knowledge of the Precambrian granitic rocks of this part of the state.

Petrographic analysis of forty-four thin sections of granitic rocks from the St. Francois Mountains area revealed six different granite types. These have been named the Fredericktown, Knoblick, Doerun, Graniteville, Klondike and Silvermine granites. These rocks form a large part of a composite batholith. More than one period of granitic intrusion is represented, but differentiation also contributed to the formation of this diversity of the rocks. In the Johannsen classification they are classified as leucogranites, granites, alaskites, kalialaskites, sodaclase granites and adamellites.

The Niggli petrochemical classification of twenty-seven chemical analyses of these granites revealed their petrogenetic relationships. The chemical character of the magma out of which they have formed was acidic, salic, relatively alkali rich and lime poor. The Doerun, Graniteville and Klondike granites are in the aplitgranitic, the Fredericktown granites and granite porphyries in the aplitgranitic and engadinitgranitic, the Knoblick granite in the granodioritic, and the

Silvermine granite in the yosemititgranitic magma type. All the rocks belong to the calc-alkalic petrographic province.

Qualitative spectrochemical analysis of forty-four granite samples revealed the presence of the following minor elements: Mg, Sr, Ba, Ti, Zr, V, Cr, Co, Ni, Cu, Ag, Zn, Sn and Pb. Mg, V, Co, Zn, Sn and Pb were selected as index trace elements. The different granite types were characterized according to the relative amounts of these. The Fredericktown granites and granite porphyries, the Knoblick granite and the Silvermine granite contain more Mg, V, and Co, and less Zn, Sn, and Pb than the other granite types. The Doerun, Graniteville and Klondike granites are also relatively high in V and Co. Zn is not always present, but they have more Sn and Pb than the other granite types. Compared with granites from other localities, the Missouri granites are characterized by a consistency of copper, a relatively frequent occurrence of tin, lead and zinc, and a rareness of chromium and silver.

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INTRODUCTION

Purpose and Scope of Investigation

Precambrian igneous and metamorphic rock units compose the basement framework of the North American continent. Large areas of these rocks are exposed in the Canadian shield. Paleozoic and younger sediments deeply cover these older formations in the basins, and thinner sections over the craton areas. In the Mid-Continent region of the United States only a limited number of outcrops of Precambrian rocks are exposed. These occur in the Black Hills of South Dakota, the Arbuckle and Wichita Mountains of southern Oklahoma, the Llano region of central Texas and the Ozark region of southeastern Missouri. In the latter area exposures of Precambrian rhyolites, felsites, granites and other igneous rocks occur in and around the St. Francois Mountains. These comprise the core of the Ozark dome.

Because a completely adequate petrographic and petrochemical study of the Precambrian granites of Southeastern Missouri had not been done, the purpose of this investigation was to petrographically identify, classify and compare the various granitic rocks of the area in hand specimens and in thin sections. New approaches for the identification and classification of the granites were attempted. In addition, chemical, petrochemical, petrogenetic, spectrochemical and geochemical methods were used in the investigation of these rocks.

Within the scope of the investigation 62 samples of granitic rocks were collected from the Southeastern Missouri igneous complex. Forty-four thin sections were analyzed, 44 spectrochemical analyses were made and 27 available chemical analyses were used for the petrochemical work.

With these new data an attempt was made to clarify the basic differences between the granite types, to establish certain rules for their recognition, and to give a new comparative basis for the determination of granite samples in general, whether from outcrops or from drill-holes in Southeastern Missouri.

Location and Size of the Area

The area of the collected samples includes most of the known Precambrian granite and granite porphyry outcrops of Southeastern Missouri. The estimated total outcrop of the granitic rocks approximates 130 square miles.

The main exposures of these rocks occur in the southern part of St. Francois County and in northern Madison County near the towns of Fredericktown and Doe Run in the St. Francois Mountains. Smaller outcrops are known at Graniteville and at Hogan in Iron County, in southeastern Washington County near Buford Mountain, in the western part of Ste. Genevieve County, in northeastern Reynolds County at Taum Sauk Mountain, in southeastern Crawford County at Viburnum, in northeastern Carter County and in certain parts of Wayne County. The index map (Figure 1.) shows the location of these outcrops.

Previous Work

One of the earliest reports which mentions the Precambrian rocks of Missouri was written by Broadhead (1874)*. In discussing the general geology of the state he recognizes the oldest rocks as granites and porphyries of Archean age. He also mentions several localities in Madison County where granite rocks may be collected.

Erasmus Haworth (1894) made the first contribution of major importance to the knowledge of the igneous rocks of Missouri. He mapped them in some detail and gave the first detailed description of the granites and granite porphyries and their geographical distribution. Chemical and mineralogical composition and texture were discussed, and three classes of the granites recognized, namely granite, biotite-granite or granitite, and hornblende-granite. The granite

*All references are in bibliography.

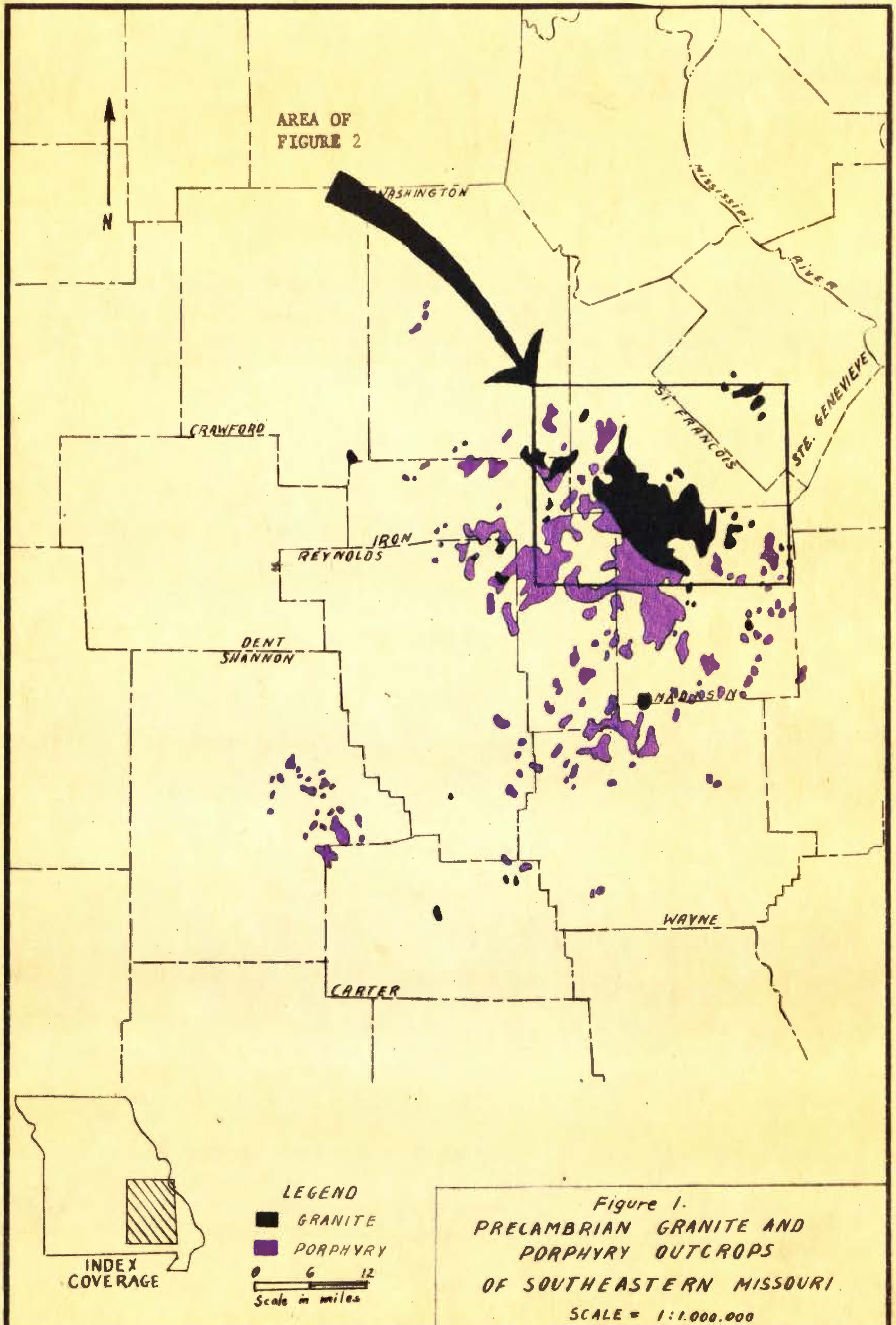

Figure 1.
PRECAMBRIAN GRANITE AND PORPHYRY OUTCROPS OF SOUTHEASTERN MISSOURI
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porphyries with feldspathic and quartzose phenocrysts were also described. Haworth concluded that the granites and granite porphyries were gradational to each other.

Keyes (1896) in an early paper discusses the relationship of the granites and porphyries of the region. He also concludes that they are closely related genetically and may be regarded as facies of the same magma.

During the next 30 years very little work was done on the Precambrian granites of Southeastern Missouri. In the 1930's interest in the subject was revived and a series of publications appeared.

Tarr (1931) submitted a paper to the Geological Society of America and presented evidence that the granites of Southeastern Missouri are intrusive into the eruptive porphyries and therefore are not of the same age.

In the following years data were accumulated to show that more than one period of intrusion was represented among the granites. On the basis of the character, amount and distribution of the heavy accessory minerals, Tolman and Koch (1936) established six different granite types, possibly representing different periods of magmatic intrusion.

Subsequently Robertson (1949) attempted the classification of the granites on a general petrographic basis. His granite types and nomenclature were accepted by the author. Robertson did little petrochemical work along the lines of the C. I. P. W. system and no spectrographic work at all. This study adds much detail which had not been considered by Robertson.

Various other reports and theses have dealt with the igneous geology of certain portions of the area investigated. Some of them contain good petrographic descriptions of these granitic rocks (French, 1956).

At present an intense interest exists by both government and industry in the Precambrian geology of Missouri. The Missouri Geological Survey is currently involved in compilation and original work on this subject.

Acknowledgements

The completion of this work was made possible through the valuable help and assistance of certain people, to whom the author expresses her thankful gratitude.

Dr. P. D. Proctor, Chairman of the Geology Department of the Missouri School of Mines, was the advisor of the thesis. He suggested the problem, supervised the work and gave the author helpful guidance and many valuable ideas. For his help in the writing the author is especially grateful. Other members of the Geology Department also cooperated in every way.

The Missouri Geological Survey gave financial assistance for the field work and for the preparation of the thin sections. The use of the facilities of the Survey is acknowledged. To members of its staff thanks are due, especially to Dr. W. C. Hayes, Assistant State Geologist, who cooperated in every way whenever his help was needed. Miss Mabel Phillips, Chemist, gave invaluable help in the spectrographic work, both in the preparation of the spectrographic plates and in the evaluation of the results.

Dr. F. G. Snyder, Chief Geologist of the St. Joseph Lead Company, contributed 10 granite samples for the purposes of the spectrographic work. Some of these are from drill-holes and served as a good comparison to outcrop samples.

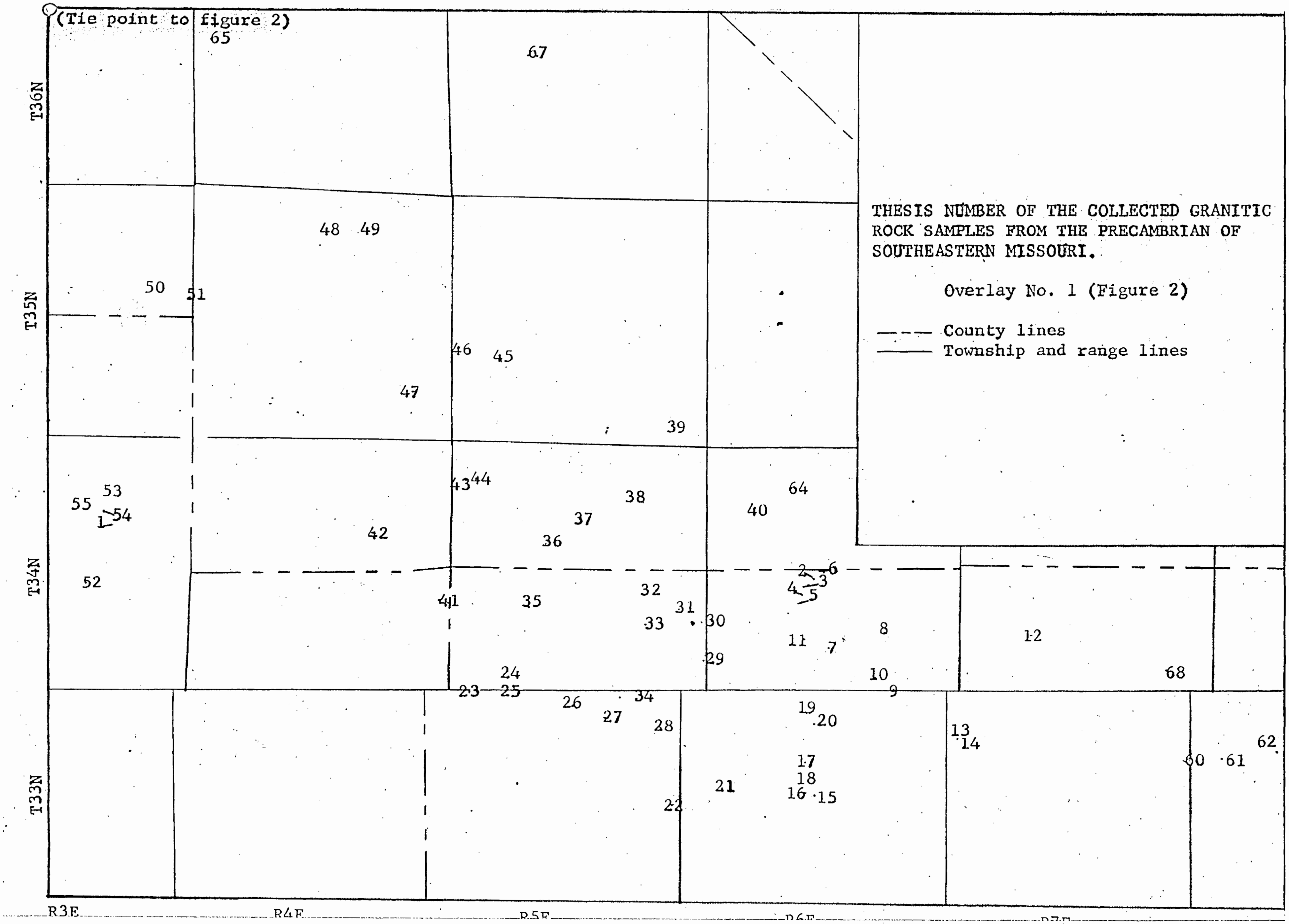
I am also very grateful for the help of my husband, Geza Kisvarsanyi, who assisted me in the field work.

METHODS OF INVESTIGATION

Field Work

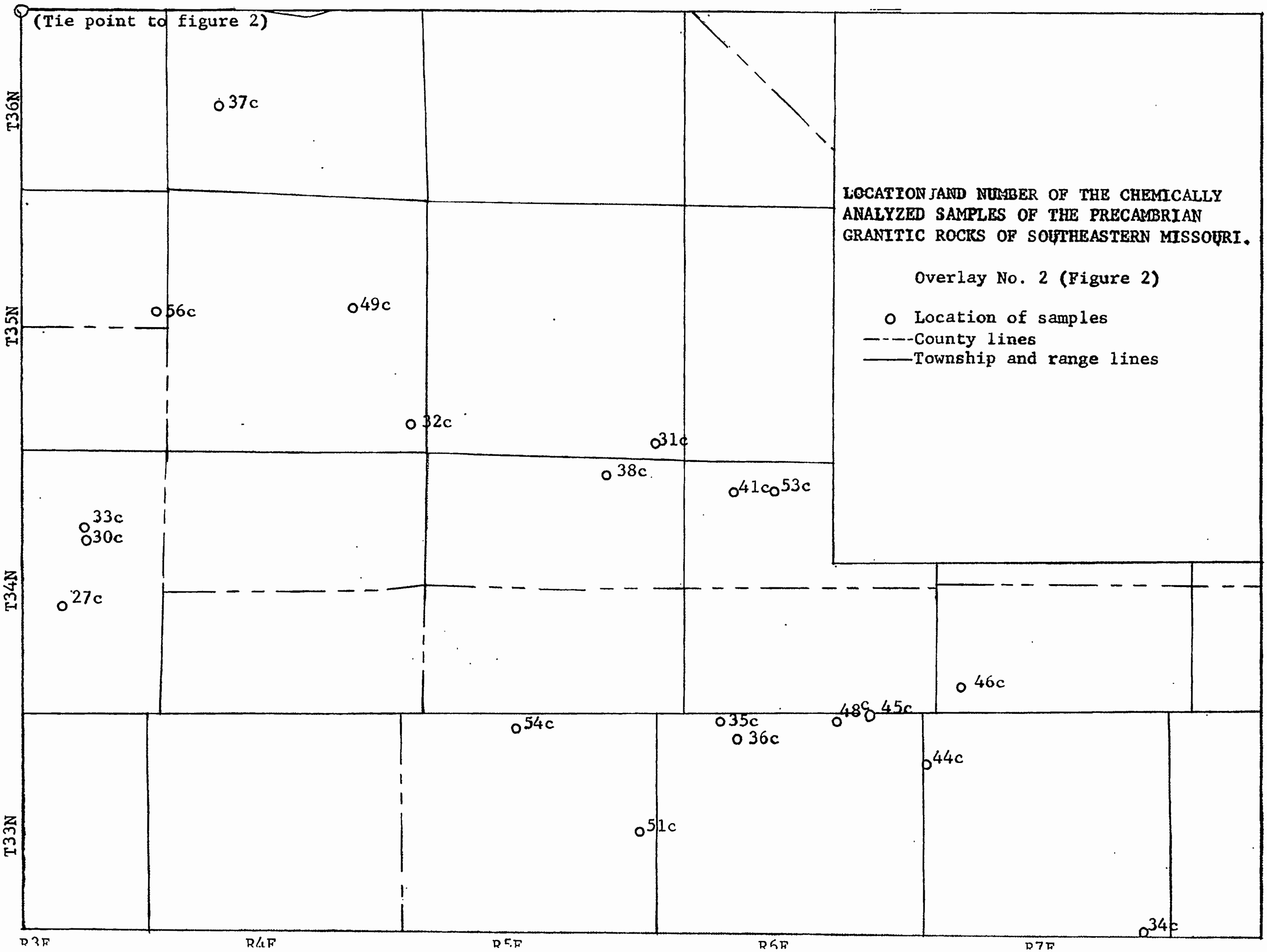
Eleven days were spent in Southeastern Missouri in the fall of 1958 and in the early spring of 1959 visiting granite and granite porphyry outcrops, quarries, and collecting rock samples. As a preparation for this work contact lines of various granite types were transferred from the unpublished Areal Geologic Map of the Precambrian Rocks of Missouri, compiled by Robertson (1949), onto 15 minute topographic sheets. With the help of these maps the granite and granite porphyry occurrences were visited wherever they were accessible. The collected samples were labeled and numbered and their locations carefully indicated on the map. Photographs were also taken of the better outcrops.

The distribution of the collected samples is shown on Figure 2. On the first transparent overlay the thesis number of the samples is indicated. The second overlay gives the location and number of the samples of the chemical analyses. Seven samples collected outside the main granite area are not indicated on this map. The exact locations of both kinds of samples are given in the Appendices. It can be noted that the numbers of the collected samples and those of the chemically analyzed samples do not correspond. The reason for this discrepancy



THESIS NUMBER OF THE COLLECTED GRANITIC ROCK SAMPLES FROM THE PRECAMBRIAN OF SOUTHEASTERN MISSOURI.

Overlay No. 1 (Figure 2)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48c
45c
54c
35c
36c
44c
51c
34c
LOCATION AND NUMBER OF THE CHEMICALLY ANALYZED SAMPLES OF THE PRECAMBRIAN GRANITIC ROCKS OF SOUTHEASTERN MISSOURI.
Overlay No. 2 (Figure 2)
o Location of samples
----County lines
——Township and range lines

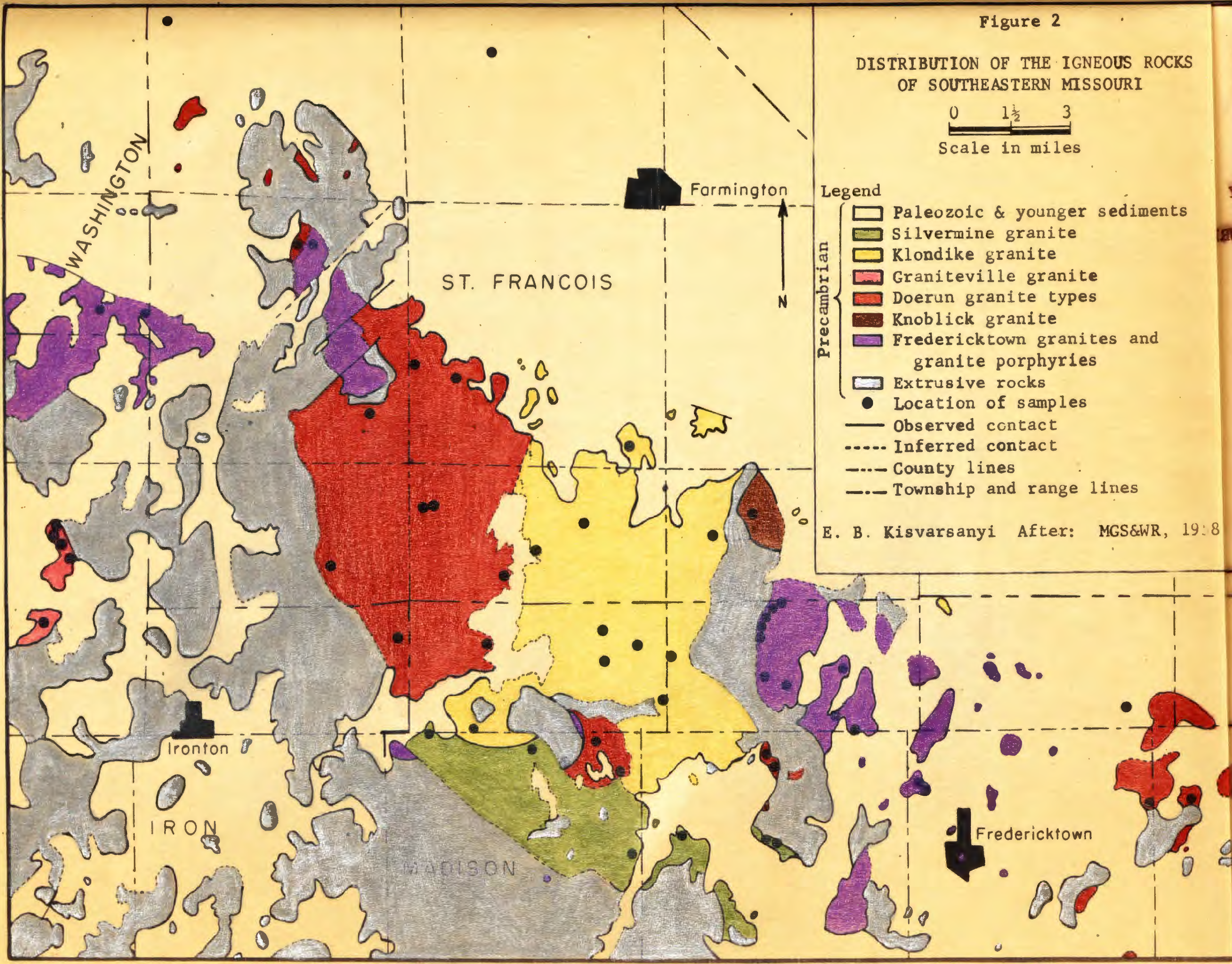
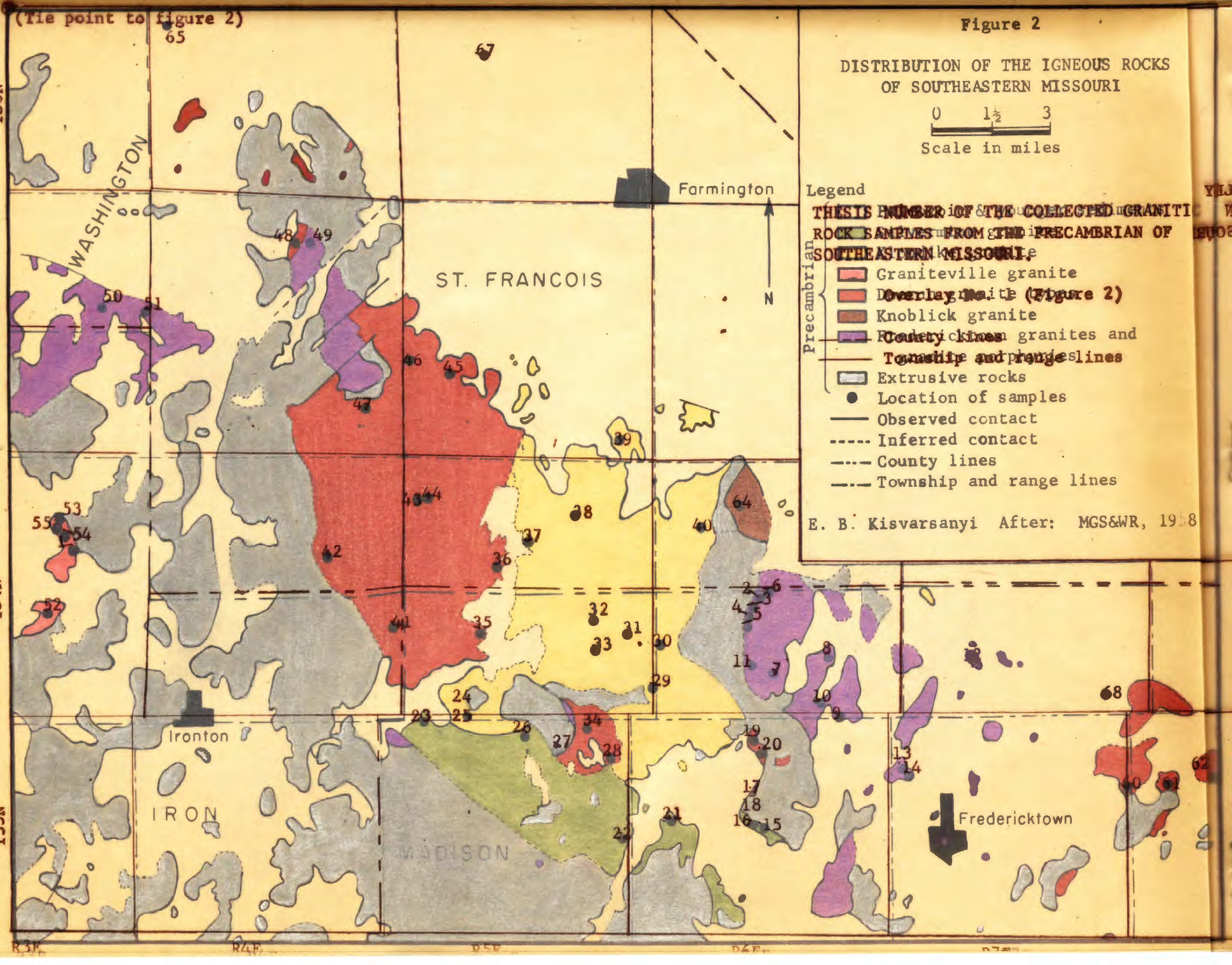


Figure 2
DISTRIBUTION OF THE IGNEOUS ROCKS OF SOUTHEASTERN MISSOURI
0 1½ 3
Scale in miles
Legend
Precambrian
Paleozoic & younger sediments
Silvermine granite
Klondike granite
Graniteville granite
Doerun granite types
Knoblick granite
Fredericktown granites and granite porphyries
Extrusive rocks
Location of samples
Observed contact
Inferred contact
County lines
Township and range lines
E. B. Kisvarsanyi After: MGS&WR, 19:8
WASHINGTON
ST. FRANCOIS
IRON
MADISON
Farmington
Ironton
Fredericktown
N
T36N
T35N
T34N
T33N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Scale in miles
Legend
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SOUTHEASTERN MISSOURI.
Overlay No. 1 (Figure 2)
County lines
Township and range lines
Precambrian
Graniteville granite
Knoblick granite
Extrusive rocks
Location of samples
Observed contact
Inferred contact
County lines
Township and range lines
E. B. Kisvarsanyi After: MGS&WR, 19 8
Farmington
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ST. FRANCOIS
WASHINGTON
Ironton
IRON
MADISON
Fredericktown
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T34N
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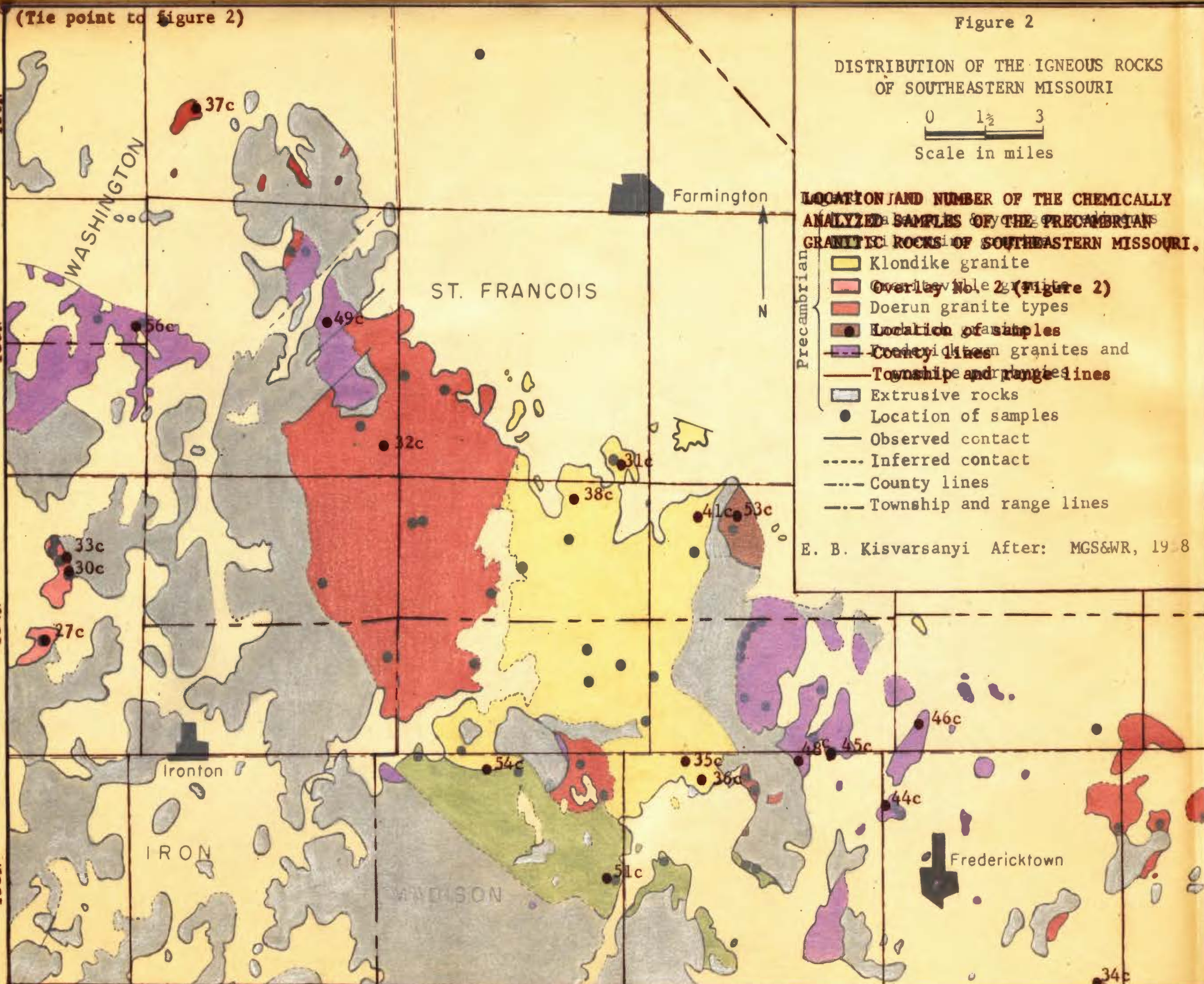
R5E
R6E
R7E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OF SOUTHEASTERN MISSOURI
0 1½ 3
Scale in miles
LOCATION AND NUMBER OF THE CHEMICALLY
ANALYZED SAMPLES OF THE PRECAMBRIAN
GRANITIC ROCKS OF SOUTHEASTERN MISSOURI.
Overlay No. 2 (Figure 2)
Location of samples
County lines
Township and range lines
Precambrian
Klondike granite
Doerun granite types
Extrusive rocks
Location of samples
Observed contact
Inferred contact
County lines
Township and range lines
E. B. Kisvarsanyi After: MGS&WR, 19 8
WASHINGTON
ST. FRANCOIS
IRON
MADISON
Farmington
Ironton
Fredericktown
N
T36N
T35N
T34N
T33N
37c
56c
49c
32c
31c
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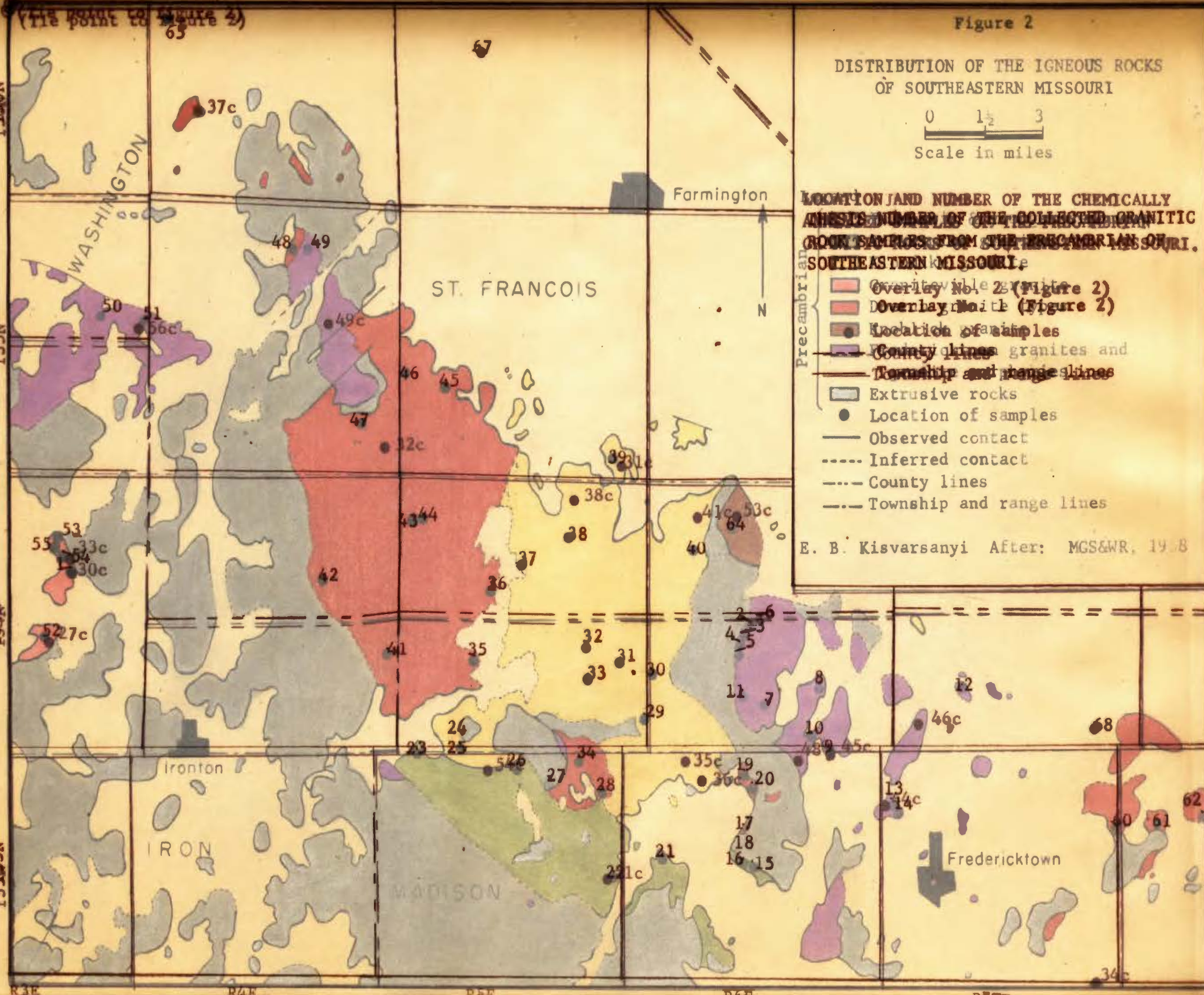
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0 1½ 3
Scale in miles
LOCATION AND NUMBER OF THE CHEMICALLY
SOUTHEASTERN MISSOURI.
Overlay No. 2 (Figure 2)
Location of samples
County lines
Township and range lines
Precambrian
Extrusive rocks
Location of samples
Observed contact
Inferred contact
County lines
Township and range lines
E. B. Kisvarsanyi After: MGS&WR
(Tie point to Figure 2)
Farmington
ST. FRANCOIS
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IRON
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MADISON
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is that the samples were analyzed prior to this investigation and already numbered. When the samples for this thesis were collected, outcrops which showed least weathering and which seemed to be most representative of the granite types were sought, instead of the old localities.

Laboratory Work

The collected samples were first studied megascopically and with the hand lens. Petrographic work on the granites and granite porphyries was done by the analysis of 44 thin sections under the petrographic microscope. The percentages of the mineral constituents were estimated, using the Rosiwal table for quantitative determination for sections considered representative of each of the granite types. Photomicrographs were prepared in the Geology Department to show characteristic textures, mineral content and unusual features of the various rocks.

Through the courtesy of the Missouri Geological Survey, 27 unpublished chemical analyses of granites and granite porphyries were made available. From these Niggli and QLM values were calculated. From these data a differentiation diagram and chemical distribution charts were prepared. A portion of the calculations was done by the author in the spring of 1958 for the Survey as a part time employee.

Forty-four of the collected rock samples were selected for spectrographic analysis. These were crushed to a fineness of about 100 mesh. They were spectrographically analyzed at the Missouri Geological Survey by Miss Mabel Phillips. Element distribution charts were prepared from these data.

GEOLOGIC SETTING

The Ozark Dome lies south of the Missouri River and includes southern Missouri, northern Arkansas and northeastern Oklahoma. It is a broad, oval upwarp with its topographic axis trending southwest through south central Missouri into Oklahoma. Precambrian igneous rocks are exposed in the Salem plateau in eastern Missouri and form the St. Francois Mountains. These comprise the core of the dome.

The igneous rocks of the area are definitely older than the overlying sediments, a fact first established beyond doubt by Haworth (1891). The absence of metamorphism along the igneous-sedimentary contacts and the presence of a basal conglomerate - often several tens of feet in thickness - containing fragments of crystalline rocks in the sedimentary strata are supporting evidences of this fact. The oldest sedimentary rocks were proved to be Upper Cambrian in age. Since igneous rocks are practically unknown in the Lower and Middle Cambrian of North America, the crystalline rocks were classed as Precambrian, possibly belonging to the Algonkian time (Proterozoic era), (Dake, 1930, p. 194).

Based on the alteration of zircon, the granites were thought to be generally younger than Huronian, as they contained mostly unaltered zircon grains (Robertson, 1949, p. 70). The latest radioactive age determinations indicate age values of 1200, 1210, and 1220 m.y. for granites and pegmatites at Graniteville and Silver Mine (Allen, 1959). If the boundary between the Archeozoic and Proterozoic eras is accepted as 1000 m.y., then these rocks should belong to the Archeozoic era and be therefore pre-Huronian.

The earliest known geologic event in the forming of the framework of this Mid-Continental structural unit was the extrusion of a great amount of rhyolitic lava. According to Dake (1930), this presumably took place in Algonkian time. The rhyolites were later intruded by granites and granite porphyries of similar chemical character. The final stage of this magmatic cycle was the extrusion of basic volcanics along major lines of weakness. Since Southeastern Missouri had a long period of erosion in Precambrian times, we can only assume that the presently observable basic dikes are the remnants of this final magmatic activity.

Later in geologic history, this part of the Precambrian craton was faulted. Some of the structural deformation was pre-Lamotte and some Precambrian. Before the invasion by the Upper Cambrian sea a long period of subaerial erosion occurred. It cut deeply into the old igneous rocks, exposed the granites, and produced a rugged topography often with a relief of 2000 feet or more.

During Paleozoic times the area was subject to successive transgressions and regressions of the sea, and deposition of sandstones, limestones, shales and other sedimentary rocks took place. The igneous rocks gradually disappeared under the thick cover of these formations and became buried hills and knobs. At the close of the Paleozoic the area slowly emerged and a second long period of erosion took place during Mesazoic and Tertiary times. During this time part of the igneous rocks were uncovered.

In the area adjacent to the granitic outcrops investigated in this study, Upper Cambrian and Lower Ordovician sedimentary rocks are present at the surface.

PETROGRAPHY AND PETROLOGY OF THE GRANITES

OF SOUTHEASTERN MISSOURI

General Statement

The granites comprise about one-third of the exposed Precambrian igneous rocks of Southeastern Missouri. The outcrops are almost exclusively in the northeastern part of the igneous area. The largest continuous granite outcrop, referred to as the main granite area, occurs in southern St. Francois and northern Madison counties. The majority of the studied samples came from this area. Numerous small granite exposures also occur outside the main granite area. These have not yet been correlated with the principal granite types of the batholith in the main granite area.

The most extensive petrologic and petrographic study of the different granite types was undertaken by Forbes Robertson (1949). He considers the different granite types as differentiates of a composite batholith emplaced as a sill-like body in essentially two phases, as follows:

The first or Fredericktown granite stage* includes

1. The Fredericktown granite* (scattered outcrops in the eastern part of the main granite area).

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*Indicates rock names not previously appearing in publications.

2. The Stono granite* (outcrops on Stono Mountain, secs. 23-26, T. 35 N., R. 4 E.).

3. The Buford granite porphyry* (outcrops on Buford Mountain and in the Wing Lake area of the northwestern part of the Ironton quadrangle).

4. The Taum Sauk granite porphyry* (outcrops in the southeastern part of the Edgehill quadrangle).

5. The Carvery Creek granite porphyry* (outcrops at Hogan Mountain, secs. 27-28, T. 33 N., R. 3 E.).

6. A group of unnamed small occurrences of similar material.

The second or Doerun granite stage* includes

1. The Doerun granite* (broad outcrop, several miles in width, extending from Doe Run Creek, south of the town of Doe Run, southward 7 or 8 miles to Brewers Creek).

2. The Graniteville granite (in the vicinity of the town of Graniteville, in Iron County).

3. The Klondike granite* (extensive outcrops just east of the Doerun granite).

4. The Jonca Creek granite* (outcrops in Ste. Genevieve County along Jonca Creek).

5. The Higdon granite* (outcrops 5 miles east of the town of Fredericktown).

6. The Silvermine granite* (outcrops in the southern part of the batholith).

7. The Knoblick granite* (small outcrop area in the vicinity of Knob Lick Mountain in St. Francois County).

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*Indicates rock names not previously appearing in publications.

The Brown Mountain rhyolite is also considered to belong to the Doerun granite stage, but as this study is restricted to the granites, it will not be further mentioned.

The majority of the names were introduced by Robertson (1949) and have not appeared in print. They are derived from geographic localities. The terms Graniteville and Silvermine granite were previously used by Tolman and Koch (1936). In the present work the above terms were adopted, although a new set of names will probably appear in a forthcoming publication of the Missouri Geological Survey.

Main Granite Types

The main granite types are discussed in the order given on the preceding page. The rock types of the Fredericktown granite stage are considered first and are followed by those of the Doerun granite stage. The two granite stages will not be separately discussed, however, in this section. The main granite types are discussed with special reference to megascopic features, textures and mineralogic composition. The latter is based on thin section analysis of the rocks. Pertinent photographs and photomicrographs showing details of these rocks are also included. The use of the terms fine, medium, and coarse-grain in respect to texture follows that of Johannsen (1939) and falls into the range of 0 to 1 mm., 1 mm. to 10 mm., and 10 mm. to 30 mm., respectively.

Fredericktown and Stono granites

Description of the Fredericktown granite also includes the Stono granite because of their similarity.

Geographic distribution. The Fredericktown granite crops out northwest of the town of Fredericktown in the eastern part of the main granite area (see Figure 2), mostly in Madison County in an area of about 15 square miles. The outcrops are scattered. The best outcrops of the Fredericktown granite were observed along Musco Creek at the Missouri Pacific Railroad, in sec. 26, T. 34 N., R. 6 E., and at the City Dam, about 1 mile northwest of Fredericktown in section 7, T. 33 N., R. 7 E. A portion of the outcrop of the Fredericktown granite along Musco Creek is shown on Plate 1.

The Stono granite occurs in the northwest part of the main granite area, nearly ten miles from the main Fredericktown granite area, in St. Francois County about two and one half miles west of the town of Doe Run. Its outcrop area is about 4 square miles and is more or less continuous.

Megascopic features. The Fredericktown and Stono granites closely resemble each other. They are fine-grained rocks, in general the finest grained of all the granites, and slightly porphyritic. Their

PLATE 1. Fredericktown granite outcrop.

Figure 1. Outcrop of the Fredericktown granite along Musco Creek in sec. 26, T. 34 N., R. 6 E., Madison County, Missouri.

color is somewhat purplish, or dark red-brown. They are very dense and hard.

Orthoclase and quartz phenocrysts are readily visible in both rock types. Pale pink orthoclase grains range to two mm. in size. Dark minerals are fairly abundant, but are of smaller size. Dark green hornblende and chlorite are present in the groundmass. Besides the dark minerals minute crystals of pale pink orthoclase are also visible. A characteristic mottled appearance of this rock type results from the association of pale pink feldspar and green femic minerals.

Texture. Microscopically the Fredericktown and Stono granites are holocrystalline, hypidiomorphic and generally slightly porphyritic. Granophyric texture is common in most of the sections, with the exception of one thin section of Stono granite.

Granophyric or micrographic texture develops when quartz crystallizes simultaneously with some other mineral, most commonly with potash-feldspar. The two minerals mutually interpenetrate, giving the resulting solid a mottled appearance. The patches of each mineral, in this case quartz and orthoclase, extinguish simultaneously over a small area in the microscope. That is, unconnected rods of quartz show simultaneous extinction and at another position of the stage of the microscope, the orthoclase masses extinguish at the same time.

Granophyric intergrowth is quite common in all the granite types of Southeastern Missouri. Myrmekitic texture refers to intergrowths of quartz and sodic plagioclase.

According to Johannsen (1939, p. 43), graphic intergrowth is generally regarded as a result of eutectic crystallization in the late stages of the solidification of a magma. Some petrologists suggest it is a replacement phenomenon. Replacement textures are not as regular or geometrically symmetrical as the usual types of eutectic origin. The absence of these features indicates that the Missouri granites are not of this type. Robertson (1949, pp. 77-78) however, notes that a replacement origin is possible for some of the granite porphyries and possibly may apply to the Fredericktown granites also.

The irregular, rather coarse, granophyric intergrowth of quartz and potash-feldspar in the Fredericktown granite is illustrated in Plate 2, Figure 1.

Mineralogical composition. Orthoclase, plagioclase, and quartz are the most abundant minerals in the Fredericktown and Stono granites. They may make up as much as 90 or 95% of the rock. Of the three, feldspars are the most abundant. Quartz averages about 25%, but often reaches 30 or 35% of the volume. Orthoclase and orthoclase-microperthite range from 35 to 60% of the rock.

PLATE 2. Granophyric and microperthitic intergrowths in Fredericktown granites.

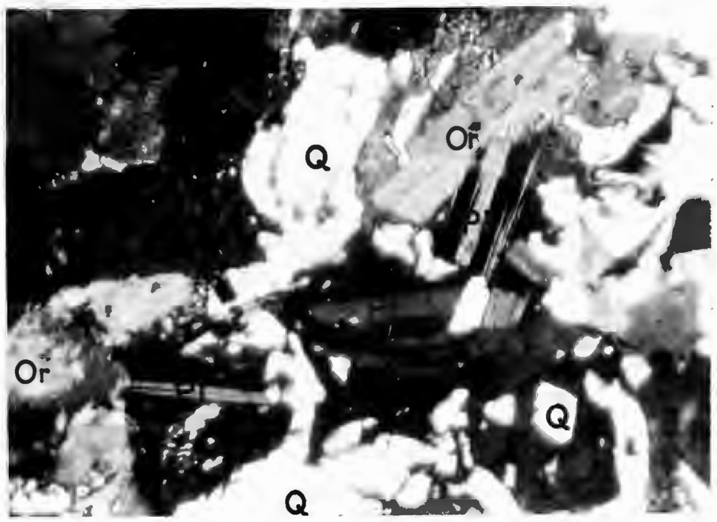


Figure 1. (x80) Granophyric intergrowth of quartz (Q) and potash-feldspar (Or) with plagioclase (Pl). (x-nicols).

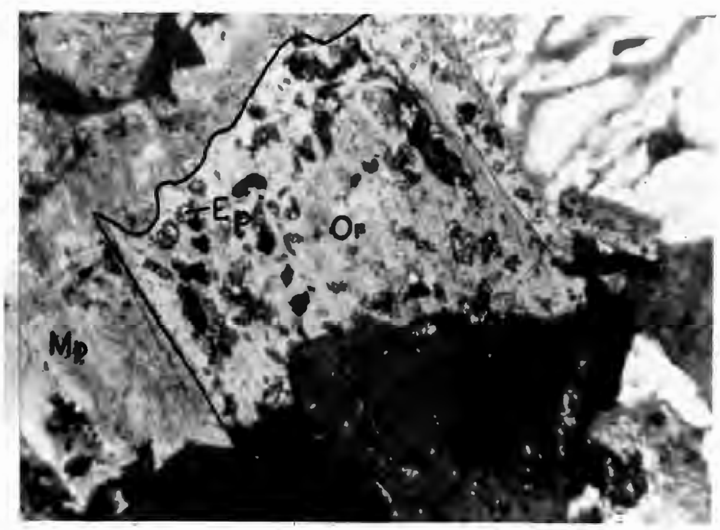


Figure 2. (x80) Microperthitic (Mp) rim around a core of orthoclase (Or). Orthoclase altered to epidote (Ep). Granophyric texture in upper right corner shows quartz (light) and orthoclase-microperthite (dark). (x-nicols).

Perthites, as defined by Winchell & Winchell (1956, Pt. II, p. 305) are "regular intergrowths of orthoclase and albite" which "are believed to be due to a secondary (unmixing) process, by which a homogeneous crystal separates (without fusion or solution) into unlike parts as a result of instability induced by cooling." Similar aggregates, composed of microcline and albite, are called microcline-perthite or microcline-microperthite.

The orthoclase and orthoclase-microperthite crystals are generally euhedral, except when contributing in the granophyric intergrowth, when both feldspar and quartz are anhedral. Orthoclase without perthitic intergrowth of albite is extremely rare. In a few cases a microperthitic outer rim was observed around an inner core of pure orthoclase (see Plate 2, Figure 2). The perthitic material probably crystallized in a later stage of the solidification process around the earlier formed orthoclase as a nucleus. The orthoclase core shows some alteration to epidote.

The potash-feldspar shows two generations. The first generation of the mineral is larger in size (1 to 2 mm.), euhedral and often has Carlsbad twinning (see Plate 3, Figure 1.). These phenocrysts lie in a finer-grained groundmass which contains a large percentage of potash-feldspar. The second generation orthoclase is smaller (0.1 to 0.5 mm.), less distinctly euhedral to subhedral and exhibits

PLATE 3. Feldspar phenocrysts in Fredericktown granites.

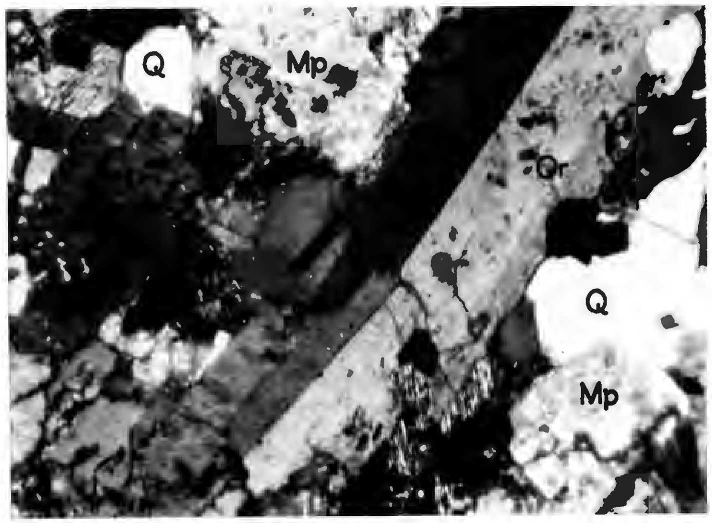


Figure 1. (x80) Carlsbad twinning in orthoclase (Or) phenocryst. Quartz (Q) and microperthite (Mp) also present. (x-nicols).

Figure 2. (x80) Plagioclase (Pl) phenocryst showing combined albitic and Carlsbad twinning. (x-nicols).

no twinning. Alteration of the large phenocrysts is generally more intense and results in sericite, clay minerals and epidote.

A few grains of microcline-microperthite were observed in one thin section of the Fredericktown granite. This mineral, however, is scarce in both granite types.

Plagioclase feldspar is less abundant than the potash-feldspar and comprises about 15% of the rock. One thin section of Stono granite showed only 2% plagioclase. The plagioclase is very sodic, although no pure albite was recognized. The Ab molecule ranges from Ab 75% to Ab 91%. The latter value was observed in Stono granite. The plagioclase rarely forms the larger phenocrysts, but when it does, the grains are euhedral and exhibit albitic twinning (see Plate 3, Figure 2). They are seldom altered. Plagioclase is more common in the finer-grained groundmass where it forms small euhedral or subhedral grains and exhibits albitic twinning. The twinning is almost always present and its presence is the easiest way to distinguish plagioclase from orthoclase. A "growth rim" may sometimes be present and produce a zoned appearance around the larger plagioclase. It is often accompanied by twinning of the main crystal. The outer narrow zone is more sodic in composition than the main crystal. According to Emmons and Mann (1953) this feature is common in the feldspars of the roof phases of granite. They cannot explain the phenomenon by conventional crystallization because of the consistent narrowness of these rims in an otherwise unzoned crystal. The solutions for these rims are supposed to be local and originate in the crystal itself, possibly during and from twinning. The formation of the rims then either may take place during twinning, in which case the rim would also be twinned, or it may be post-twinning, in which case the rim would not exhibit twinning, as in the case of the Southeastern Missouri granites. Since twinning develops late in the growth of a crystal, an untwinned growth rim indicates an even later event in the crystallization. The phenomenon, however, was rare in the granites of Southeastern Missouri. It was observed only in a few marginal samples of the Fredericktown granite, and may reflect smaller local conditions.

Hornblende and chlorite were recognized in the Fredericktown granite. Their amount varies between 5 and 10%. Chlorite is generally more abundant. Green hornblende occurs in small euhedral to subhedral grains. It is pleochroic in yellowish green and bluish green, sometimes in green and brown. The grains are often altered to chlorite. Most of the chlorite is thought to be deuteric alteration of former ferromagnesian minerals, notably hornblende and possibly biotite. No biotite was recognized in any of the sections.

In Stono granite about 10% green hornblende was present. Numerous inclusions of apatite and closely associated magnetite (see Plate 4,

Figure 1) occurred with it. Alteration of the hornblende to chlorite was less pronounced. A small amount of biotite was also recognized.

The non-magnetic heavy accessory mineral suite of these granites consists of fluorite, apatite and some zircon. The latter was recognized only in sample No. 6. The zircon forms inclusions in hornblende, but shows no pleochroic halos. Apatite is fairly common as inclusions in both feldspar and hornblende (Plate 4, Figure 1). In the Stono granite some purple fluorite occurred as inclusions in feldspar. The epidote always appears as an alteration product of feldspars (Plate 2, Figure 2).

Magnetite is present in most sections as small euhedral grain inclusions in quartz, feldspar and hornblende. It is believed to be primary. Iron oxides (magnetite and hematite) occur in close association with altered ferromagnesian minerals as irregular clusters and grains. The optical relationship and alteration pattern suggests that these minerals were formed during the decomposition of the ferromagnesian minerals.

Plate 4, Figure 2 illustrates a peculiar feature of the Stono granite. In a small area of the thin section a wedge-shaped fracture was recognized which was completely filled with a fine-grained material. The composition of this fine-grained filling is mostly potash-feldspar and embedded in it is a large number of small, mostly euhedral magnetite grains. Figure 2 is at the border of the two kinds of materials

PLATE 4. Microscopic features of Stono granite.

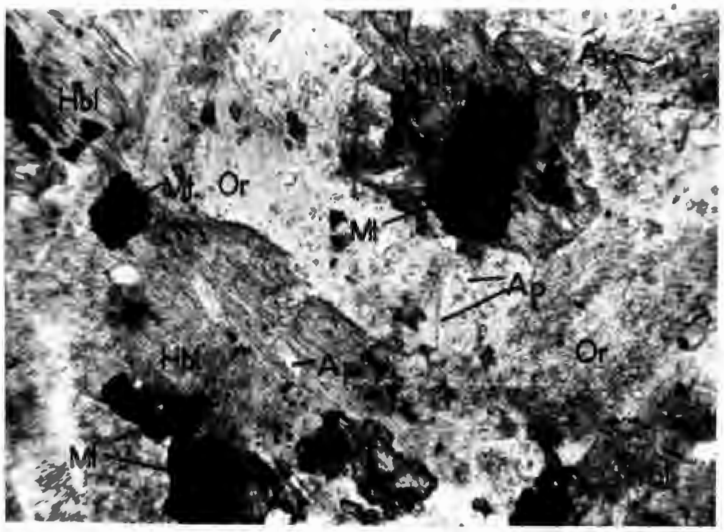


Figure 1. (220x) Inclusions of apatite (Ap) and magnetite (Mt) in orthoclase-microperthite (Or) and hornblende (Hbl). (Parallel nicols).

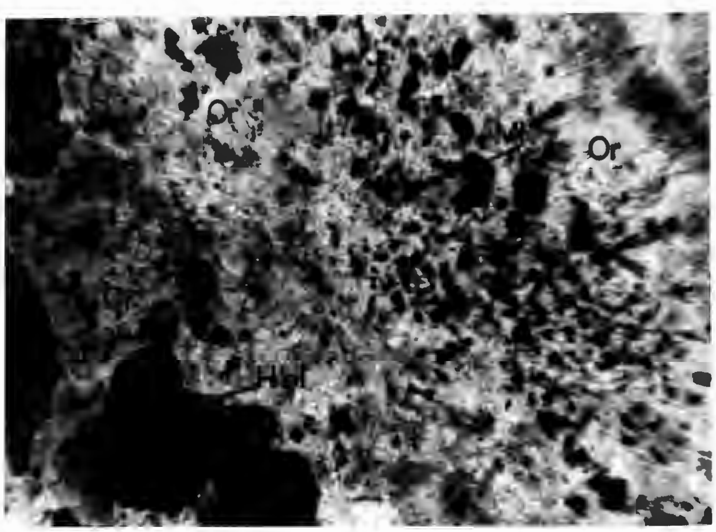


Figure 2. (140x) To the right: fracture filling material composed of potash-feldspar (Or) and magnetite (Mt). To the left: hornblende (Hbl) and potash-feldspar (Or) of the rock.

with the fracture trending northwest on the left side of the photomicrograph. Larger grains of hornblende and potash-feldspar occur to its left. Fredericktown granite is illustrated in Plate 5, Figure 1.

Granite porphyries

Geographic distribution. Three different types of granite porphyries are located in three different areas. All of them occur west of the main granite area. In Figure 2 only the Buford granite porphyry outcrops are shown. The latter comprises about ten square miles in the southeastern part of Washington County, northeastern Iron County and western St. Francois County about three miles north of Graniteville.

The Carvery Creek granite porphyry crops out at the base of Hogan Mountain, in sections 27 and 28, T. 33 N., R. 3 E., in an area of less than one square mile about six miles southwest of Ironton.

The Taum Sauk granite porphyry outcrops are about ten miles west and southwest of Ironton, on both sides of the East Fork of Black River. The outcrop area is approximately five square miles. Unfortunately no sample was obtained from this area.

Megascopic features. The Buford granite porphyry is a very fine-grained, dense, dark brown, porphyritic rock. Phenocrysts of orthoclase and quartz range from 1 to 3 mm. in size, but the groundmass is microcrystalline.

PLATE 5. Grain size relationship in the Fredericktown granite and the Buford granite porphyry.

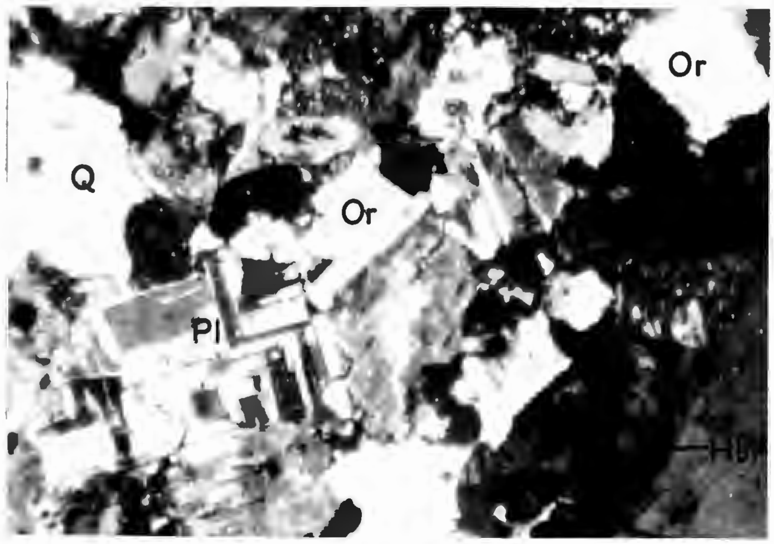


Figure 1. (x80) Fredericktown granite with quartz (Q), plagioclase (Pl), potash-feldspar (Or) and hornblende (Hbl). (x-nicols).

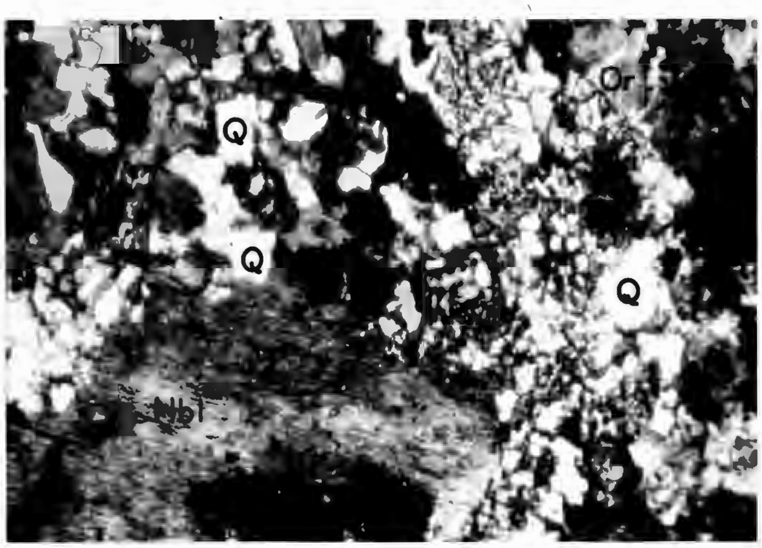


Figure 2. (x80) Two grain sizes in the groundmass of the Buford granite porphyry. The phenocryst is hornblende (Hbl). The groundmass is composed of potash-feldspar (Or), quartz (Q) and hornblende. (x-nicols).

The Carvery Creek granite porphyry consists of a dark gray microcrystalline groundmass which contains large phenocrysts of pale pink orthoclase, some of which may be over five mm. in size. The rock is distinctly porphyritic.

Texture. Both rock types are holocrystalline and porphyritic. Larger phenocrysts are embedded in finer grained groundmass.

In the Buford granite porphyry the groundmass is fine-grained granular, granophyric texture is not well developed. An interesting feature of the texture of the granite porphyry is well illustrated in Plate 5, Figure 2. A large phenocryst of hornblende occurs in the lower part of the photomicrograph. A coarser grained phase of the groundmass is visible in the upper left portion and a much finer grained phase occurs to the right. The individual grain size in the coarser phase may be three or four times as large as that in the finer phase. The latter is more abundant. A very delicate development of granophyric intergrowth is present in the upper part of the figure, just to the right of the coarser phase. Note that the border between the two phases is not sharp. A poikilitic texture is sometimes present in the Buford granite porphyry.

The two granite porphyries exhibit certain differences in crystallinity. The Carvery Creek granite porphyry is more crystalline. It also has large phenocrysts like the Buford granite porphyry, but the character of the groundmass is different. The groundmass of the Carvery Creek granite porphyry is much coarser, but the individual grains have a very fine-grained granophyric texture. Because of this, the groundmass actually looks finer grained. Poikilitic texture was not observed in this rock type.

Mineralogical composition. Phenocrysts comprise about 25% of the Buford granite porphyry. They vary in size from 1 to 3 mm. and include orthoclase, orthoclase-microperthite, quartz, and hornblende. The potash-feldspars are euhedral and subhedral; some of them are strongly sericitized. Inclusions of hornblende, fluorite, apatite and zircon, and sometimes quartz may be present. Quartz phenocrysts occur in euhedral, subhedral and anhedral forms. They are generally smaller in size than the feldspars and often show corrosion of the rim. Inclusions in quartz are zircon and sometimes potash-feldspar. Minor chloritic alteration of the hornblende is present. Magnetite and apatite often form inclusions in the latter (see Plate 6, Figure 1).

The mineralogical composition of the two groundmass types of the Buford granite porphyry is different. In the coarser phase potash-feldspar, plagioclase, quartz and hornblende are present, the finer phase is composed dominantly of quartz and some potash-feldspar (see Plate 5, Figure 2).

Accessory minerals in the Buford granite porphyry are apatite, zircon, fluorite and magnetite. Secondary iron oxides (magnetite and hematite) are probably alteration products of hornblende.

In the Carvery Creek granite porphyry the phenocrysts are large potash-feldspars (1 to 5 mm. in size) and green pleochroic hornblende. The feldspars are euhedral and subhedral. Sericitic alteration is quite common. Plate 6, Figure 2 illustrates a large potash-feldspar phenocryst with distinct zoning. Small inclusions of quartz are visible to the left. The hornblende is euhedral and subhedral, some of it is altered to chlorite and magnetite.

The groundmass of the Carvery Creek granite porphyry is almost entirely granophyric and composed of quartz and orthoclase-microperthite with small patches of hornblende and magnetite. The accessory minerals are apatite as inclusions in hornblende, fluorite and magnetite.

Doerun granite

Several of the outlying red granites such as those from Viburnum and Higdon belong to the Doerun mineralogical type, but these will be discussed separately. In the following section only the Doerun granite proper, with its outcrops in the main granite area, will be considered.

PLATE 6. Microscopic features of the Buford and Carvery Creek granite porphyries.

Figure 1. (x80) Hornblende (Hbl) phenocryst in Buford granite porphyry with inclusions of apatite (Ap) and magnetite (Mt). The groundmass is the fine-grained variety composed mainly of quartz. (normal light).

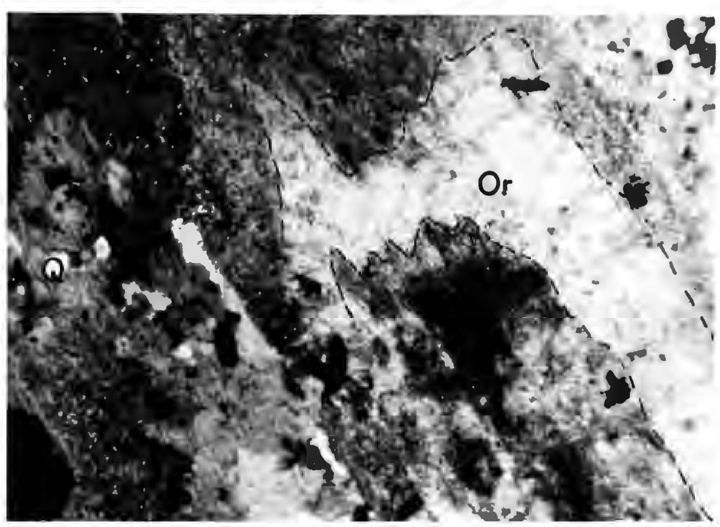


Figure 2. (x80) Distinct zoning in large potash-feldspar (Or) phenocryst in Carvery Creek granite porphyry. Small inclusions of quartz (Q) on left. (x-nicols).

Geographic distribution. The outcrop of the Doerun granite type occupies the western part of the main granite area and extends from Doe Run Creek south of the town of Doe Run southward to Brewers Creek. It is a large continuous outcrop seven or eight miles long of north-south trend and up to 5 miles wide. The total outcrop area is about thirty square miles. An isolated smaller outcrop of this granite lies within the main grainite area southwest from Bevos Mountain in Madison County where it occupies an area of about two square miles in sections 1 and 2, T. 33 N., R. 5 E. Small outcrop areas also occur in sections 3 and 4, T. 33 N., R. 6 E.

Megascopic features. The Doerun granite is distinctly red and is a fine to medium-grained rock which may be slightly porphyritic with phenocrysts of flesh-colored orthoclase and quartz. The rock contains very minor femic minerals and is essentially composed of orthoclase and quartz. According to Forbes Robertson (1949, p. 107), miarolitic cavities lined with quartz, femic minerals and fluorite are not uncommon.

Texture. The Doerun granites have a holocrystalline, hypidiomorphic and generally equigranular texture. Occasionally larger porphyritic grains of orthoclase and quartz may be present.

Granophyric texture was observed in samples Nos. 41, 45, 46, and 47. The widest range of development of this texture occurs in

Nos. 45 and 46. In both samples about 65% of the rock has a granophyric texture. Figures 1, 2 and 3 of Plate 7 illustrate some of the more interesting developments of the micrographic intergrowth in these sections. Figure 1 shows a common phenomenon with branch-like quartz blebs radiating outward toward the margin of feldspar grain. This may be called the "radial-type" of granophyric texture. A "parallel-type" of granophyric intergrowth is visible in Figure 2. To the right and above a large quartz grain, quartz blebs with parallel arrangement occur within the feldspar. Figure 3 illustrates a coarser and more irregular pattern. Triangular and polygonal quartz blebs are arranged somewhat haphazardly within the potash-feldspar. Myrmekitic texture was not observed in these thin sections.

In samples Nos. 41 and 47 less variety of the granophyric intergrowth was observed. Here it was not as dominant and comprised perhaps 30% of the rock. The intergrowth of quartz and potash-feldspar is not complete, but is mainly present at the peripheral areas of the larger quartz grains. In places it occurs as almost parallel inclusions of feldspar in the quartz. The intergrowth is coarser grained and not so regularly developed in these samples.

No granophyric texture was observed in samples Nos. 28, 34, 35, 36, 43 and 44. This is in accordance with the observation of Robertson (1949, p. 75), who found that the widest range of granophyric textures developed in the marginal facies of the granite.

PLATE 7. Various types of granophyric texture in Doerun granite.

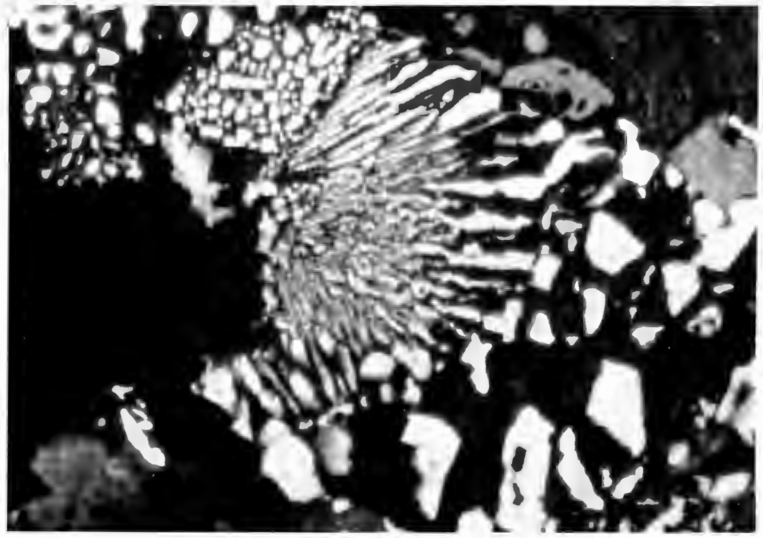


Figure 1.

(x80) Radial type. Quartz (light), potash-feldspar (dark).

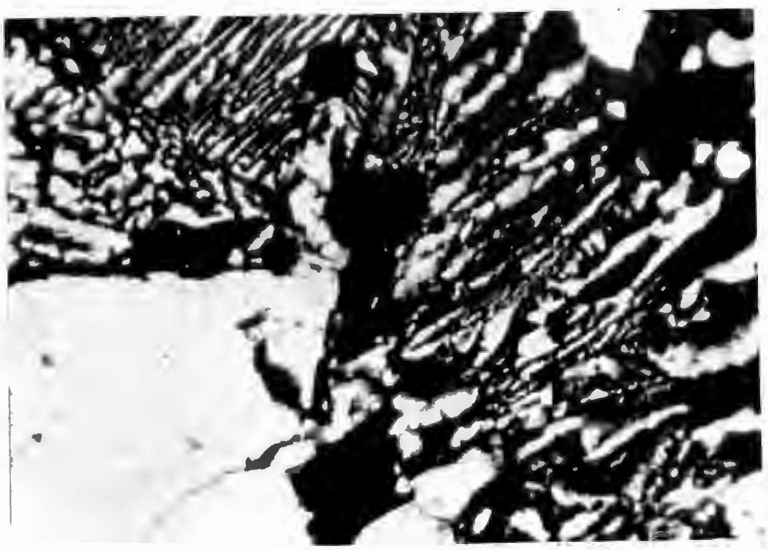


Figure 2.

(x80) Parallel type. Quartz (light), potash-feldspar (dark).

Figure 3.

(x80) Coarse grained type. Quartz (light), potash-feldspar (dark).

A small inclusion was observed in sample No. 36 (see Figures 1 and 2, Plate 8). The inclusion is composed of feldspar (plagioclase), and some biotite and magnetite. It may be a xenolithic inclusion, or an earlier, more basic product of the crystallization.

Mineralogical composition. The essential primary minerals of the Doerun granite are orthoclase-microperthite and quartz. The former often reaches 55-60%, the latter sometimes 40-45% of the rock volume. The feldspar is usually euhedral or subhedral and frequently shows Carlsbad twinning. The grains may show sericitic alteration. In the samples previously mentioned the potash-feldspar and quartz occur together in the granophyric intergrowth and comprise from 30 to 65% of the rock. Microcline-microperthite may occasionally comprise 1-2% of the mineral content.

Plagioclase is generally less common in the Doerun, than in the Fredericktown granite. It varies in amount from practically zero in the samples Nos. 45, 46 and 47, to 10% but is generally less than 5%. Only in sample No. 36 did the amount of plagioclase reach almost 25%, the potash-feldspar comprises 35% of the rock. The plagioclase grains are usually euhedral, small, and exhibit albitic twinning. The Ab molecule varies from 86% to 94%. The larger grains appear more albitic in composition, while the smaller ones approach oligoclase.

PLATE 8. Xenolithic inclusion in Doerun granite.

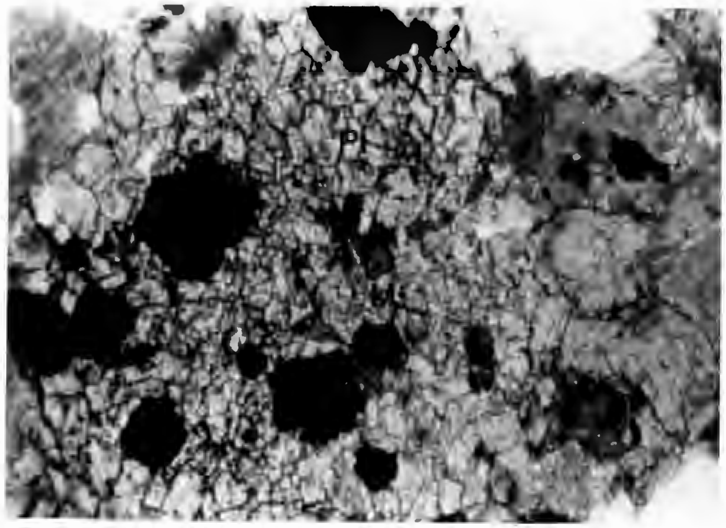


Figure 1. (x80) Possible xenolithic inclusion in Doerun granite. Plagioclase (Pl), magnetite (Mt.) (normal light).

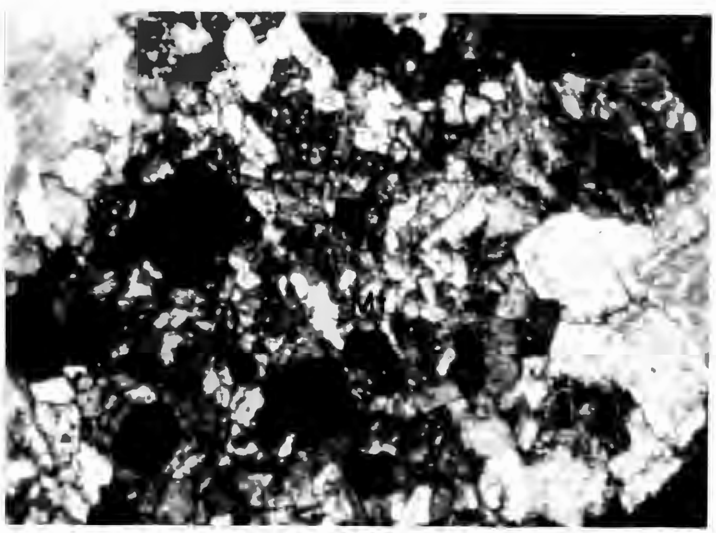


Figure 2. (x80) Possible xenolithic inclusion in Doerun granite. Plagioclase (Pl), magnetite (Mt). (x-nicols).

The femic mineral group is composed of biotite and chlorite and rarely exceed 3% in amount. Chlorite is the alteration product of the biotite. Some serpentine also occurs as an alteration product. The femic minerals occur in small euhedral and subhedral grains. The biotite is pleochroic in dark green and yellowish green. No hornblende was recognized.

The accessory minerals include fluorite, zircon and magnetite. Fluorite is the most abundant and forms inclusions in quartz and potash-feldspar. It occurs both in colorless and purplish variety. Zircon usually is present as minute inclusions in quartz, although in sample No. 43 it forms a small aggregate with magnetite and quartz in orthoclase-microperthite. Magnetite is rare as primary crystallization product, while secondary magnetite commonly occurs as an alteration product of the ferromagnesian minerals.

Graniteville granite

Geographic distribution. The outcrops of the Graniteville granite occur in Iron County, west of the town of Graniteville, in sections 10, 11, 14, 15 and 22, T. 34 N., R. 3 E. Two small isolated outcrops are visible, each less than one square mile in area. The Graniteville granite is the famous "Missouri red granite" which has been extensively quarried and used as building material throughout the United States.

Sheahan quarry, in section 11, T. 34 N., R. 3 E., one of the most active in the district, is shown in Plate 9, Figure 1.

Megascopic features. The Graniteville granite is a medium to coarse-grained, fairly equigranular, reddish rock. Orthoclase and quartz crystals may attain 10-15 mm. in size or more. The rock also contains biotite and muscovite flakes. The typical coarse-grained texture of the granite is well shown in Plate 9, Figure 2. This is a fresh rock surface in Sheahan quarry. Besides the dominant reddish variety another variety was recognized in outcrop in the SE 1/4, NE 1/4 section 10, T. 34 N., R. 3 E., at the roadside. It was only a few square feet in size. It is darker and somewhat purplish, but in grain size and mineral composition is similar to the rest of the Graniteville granites. Nothing could be learned of its relationship to the red granites.

Pegmatitic mineralization of the Graniteville granite in Sheahan quarry is described in detail by Tolman and Goldich (1935). They recognize topaz and beryl among the minerals of the pegmatite vein. A few granite samples from the quarry showed pyrite, chalcopyrite and quartz on joint planes.

Weathering of the Graniteville granite produced the well known "elephant rock" forms just west of Graniteville (see Plate 10, Figure 1.). Joint planes traverse the rock, breaking it up to form prismatic blocks in the granite.

PLATE 9. Outcrop and megascopic appearance of the Graniteville granite.

Figure 1. Quarry operation in the Graniteville granite, Sheahan Quarry, Iron County, Missouri, looking northeast.

Figure 2. Fresh rock surface of the Graniteville granite from the Sheahan Quarry.

Texture. The Graniteville granite has a holocrystalline, hypidiomorphic texture. It is fairly equigranular, although sometimes, as in sample No. 53, large phenocrysts may occur in a coarse, crystalline matrix. The porphyritic texture is illustrated in Plate 10, Figure 2. No granophyric texture was recognized in any of the samples.

Mineralogical composition. Of the essential minerals potash-feldspar occurs in two forms: as orthoclase-microperthite and as microcline-microperthite. The former comprises from 25 to 40% of the rock, the latter from 20 to 50%. They usually occur as large grains of euhedral and subhedral form and contain several inclusions. Carlsbad twinning is frequently present. Only a few of the crystals show sericitic alteration. Figure 1 of Plate 11 shows muscovite inclusions in orthoclase-microperthite. This is an interesting phenomenon of this granite type. According to Tolman and Goldich (1935) the muscovite replaces the feldspar. The examined samples in which this phenomenon occurred were very fresh. The muscovite seemed to be arranged at random within the feldspar. Since the chemical composition of the two minerals are almost identical, they may well have crystallized at the same time.

Plagioclase comprises about 18 to 20% of the rock. It occurs mostly as euhedral grains and contains numerous inclusions. The composition varies from Ab 86% to Ab 96%. Albite twinning is commonly

PLATE 10. Weathering and textural phenomena of the Graniteville granite.

Figure 1. "Elephant rock", Graniteville, Missouri.

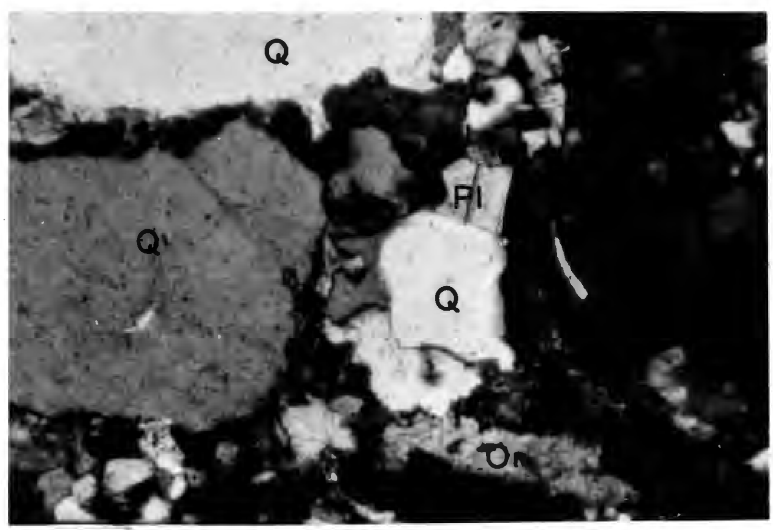


Figure 2. (x80) Porphyritic texture in Graniteville granite. Quartz (Q), potash-feldspar (Or), plagioclase (Pl). (x-nicols).

present. A large plagioclase grain with distinct albitic twinning within microcline-microperthite is illustrated in Plate 11, Figure 2.

Quartz makes up from 25 to 35% of this granite. It is usually anhedral and varies in size from 0.5 to 10 mm. Inclusions of mica and feldspar are common.

Biotite and muscovite comprise the rest of the essential mineral suite. Both minerals vary in amount between 1 and 10%, their total percentage is not less than 5%. The biotite is green, not distinctly pleochroic, and occurs as small euhedral and subhedral grains. Tolman and Goldich (1935, p. 231) describe the "green biotite" as an alteration product of biotite. Muscovite occurs in two forms: as individual larger grains and as small inclusions in the feldspar. Tolman and Goldich (1935) suggest that the muscovite is deuteric and was derived from an earlier iron bearing mineral, such as biotite, by the action of late magmatic juices. The liberated iron would be fixed as magnetite. No evidence was found in the slides examined to support this possibility. Plate 12, Figure 1 illustrates a large muscovite (M) grain in association with plagioclase (Pl), quartz (Q), and orthoclase-microperthite (Or). There is no sign of the "fixed magnetite". The muscovite is thought to be primary.

Fluorite is the most abundant accessory mineral. In one thin section it represents 2% by volume of the rock. It is usually euhedral, sometimes subhedral and mostly purplish in color. It occurs as

PLATE 11. Feldspars and muscovite in Graniteville granite.

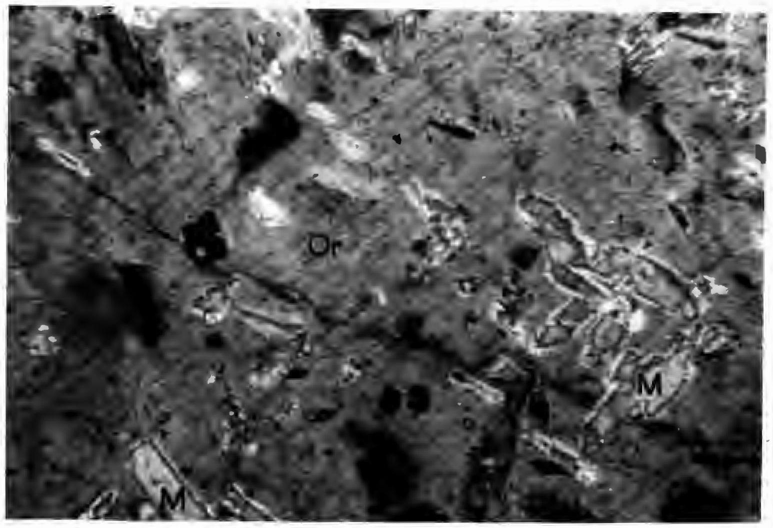


Figure 1. (x220) Muscovite (M) inclusions in orthoclase-microperthite (Or) in Graniteville granite. (xnicols).

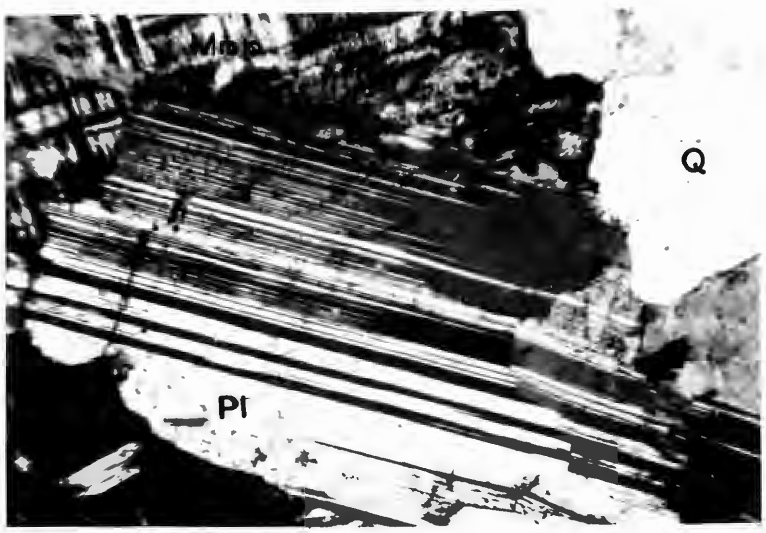


Figure 2. (x80) Plagioclase (Pl) in microcline-microperthite (Mmp) in Graniteville granite. Quartz (Q) is also visible. (x-nicols).

inclusions in quartz and feldspar and may form small aggregates with magnetite and hematite. Figures 1 and 2 of Plate 13 illustrate a large fluorite inclusion in orthoclase-microperthite between parallel and crossed nicols, respectively. Apatite, magnetite and hematite comprise the rest of the accessory mineral suite. Tolman and Koch (1936) also report the presence of zircon, green spinel, cassiterite and molybdenite as rare constituents of the accessory mineral suite of the Graniteville granite. These were not recognized in the three sections studied. Fluorite and apatite associated with muscovite in biotite are shown in Plate 12, Figure 2.

Klondike granite

Geographic distribution. The Klondike granite crops out in the middle of the main granite area, east of the Doerun, west of the Fredericktown and north of the Silvermine granite outcrops, in St. Francois and Madison Counties. The outcrops cover approximately thirty-three square miles.

Megascopic features. The Klondike granites show a wider range in megascopic appearance than any of the other granite types. On the west the Klondike granite seems to grade into the Doerun granite, while on the south, in the vicinity of Roselle in section 31, T. 34 N., R. 5 E.,

PLATE 12. Mineral associations in Graniteville granite.

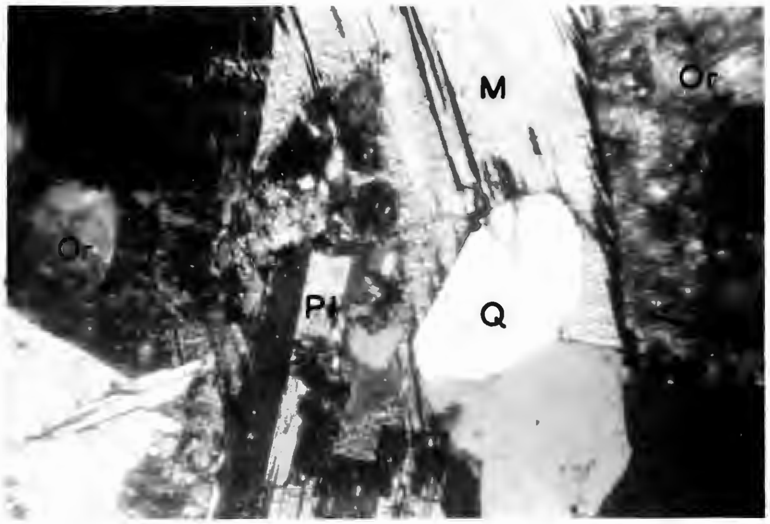


Figure 1. (x60) Muscovite (M) in association with plagio-clase (Pl), quartz (Q) and orthoclase-microperthite (Or). (x-nicols).

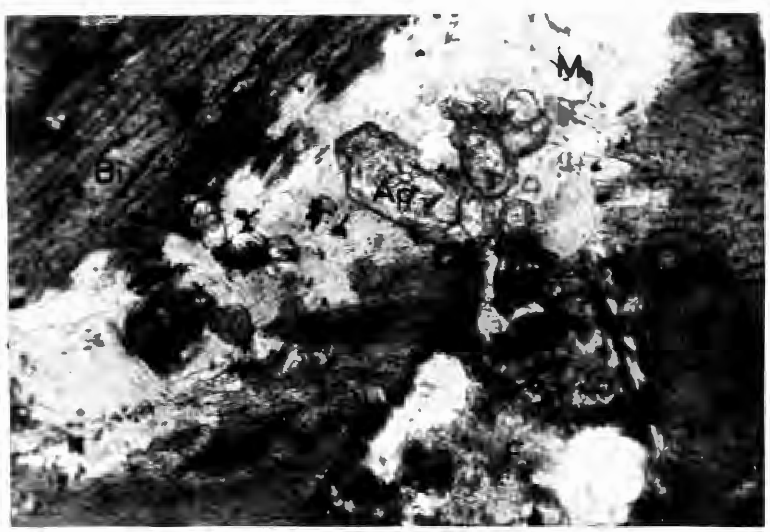


Figure 2. (x220) Fluorite (F) and apatite (Ap) associated with muscovite (M) in biotite (Bi). (normal light).

PLATE 13. Fluorite inclusion in Graniteville granite.

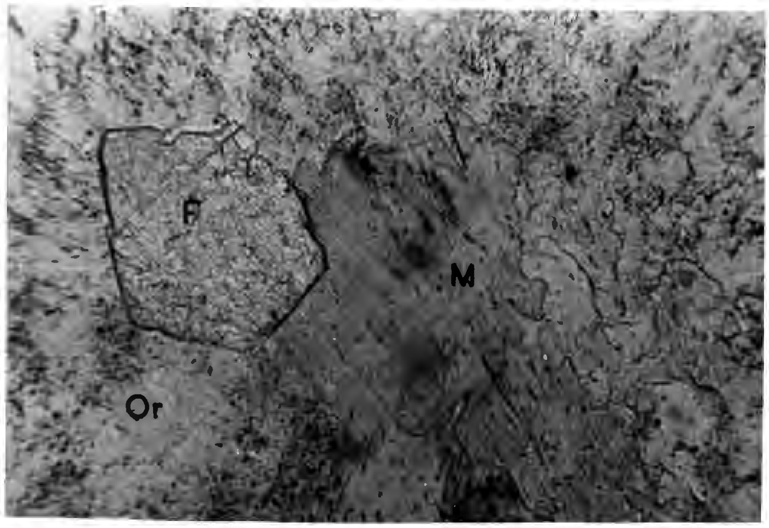


Figure 1. (x220) Fluorite (F) inclusion in orthoclase-microperthite (Or), with muscovite (M). (normal light).

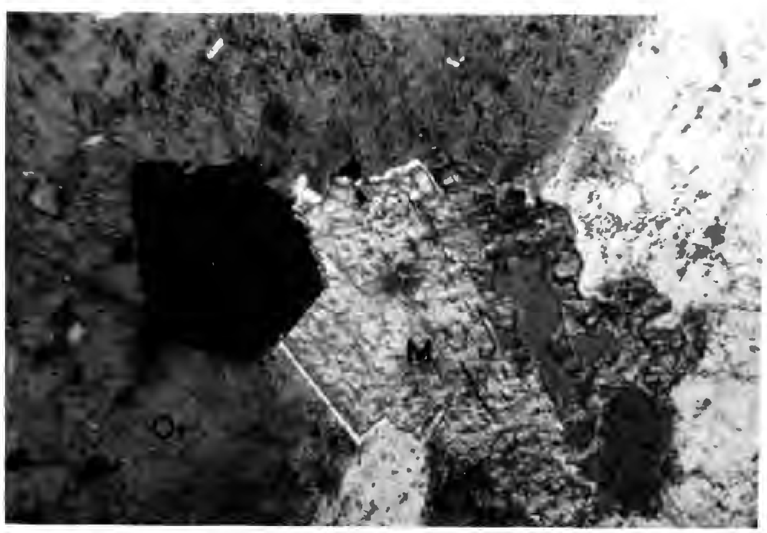


Figure 2. (x220) Same as above with crossed nicols.

its transition into the Silvermine granite can be observed. Sample No. 37, for example, closely resembles a typical Doerun granite. It is medium-grained, reddish, and composed mainly of orthoclase and quartz with very minor dark minerals. Samples Nos. 38, 39 and 40, respectively, become paler in color through different shades of pink to the light gray color of sample No. 40. The color change is due partly to the increasing amount of plagioclase, partly to the coloring of the orthoclase itself. The amount of dark minerals shows a slight increase toward the east. Sample No. 24 at the south end of the granite mass more closely resembles the Silvermine granite than any of the other Klondike samples. However, its transition to the former is more evident microscopically, as will be commented upon later. In the intermediate zone medium-grained, light pink granites are prevalent.

Texture. The Klondike granites show a wide range in grain size. The most coarse grained sample was collected in the vicinity of Roselle. Generally these granites are fine and medium-grained, holocrystalline and hypidiomorphic. Equigranular texture is more common, and even if porphyritic texture is present, it is never as pronounced as in the case of some other granite types. Granophyric texture is present in samples Nos. 37, 38, 39 and 40, and absent in the others. However, the abundance and variety of this texture, as observed in some of the Doerun granites, is not recognized here. Figure 1 of Plate 14 illustrates the granophyric texture in the Klondike granite.

Mineralogical composition. Orthoclase-microperthite is the most abundant mineral and ranges in amount from 40 to 60%. Samples Nos. 24 and 40 contain generally less of it than the rest of the granites. Both euhedral and subhedral grains were observed; some showed Carlsbad twinning. Inclusions of plagioclase, femic minerals and apatite are common in the perthite. Some of the larger grains show advanced sericitic alteration. Some epidote may also be present as an alteration product. Microcline-microperthite was observed only in samples Nos. 24 and 39, where it comprises 2 and 5% of these rocks, respectively.

Plagioclase is almost always present, though in greatly varying amounts. Through samples Nos. 37-40 it varies from 2 to 30%; in sample No. 24 it comprises about 25% of the rock; in the rest of the samples it varies from 10 to 20%, without much apparent regularity. The composition of the plagioclase varies from Ab 85% to Ab 95%. Usually two generations of the mineral can be recognized. The earlier formed larger euhedral grains show a marked zonal alteration to sericite in sample No. 24. The small euhedral grains of the second generation are usually fresh. Albitic twinning is common in both. In some fresh plagioclase grains several inclusions of lamellae-like sericite occur in a parallel arrangement with the twin planes.

PLATE 14. Textural and mineralogical features of the Klondike granite.

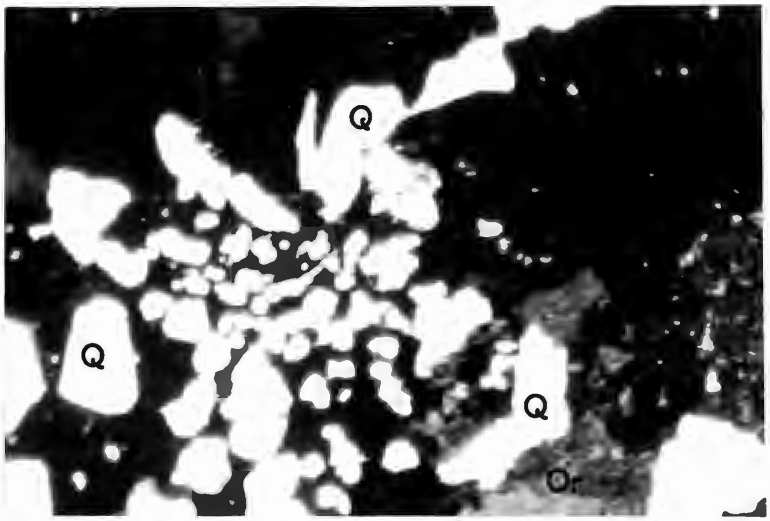


Figure 1. (x80) Granophyric texture in the Klondike granite. Quartz (Q), orthoclase-microperthite (Or). (x-nicols).

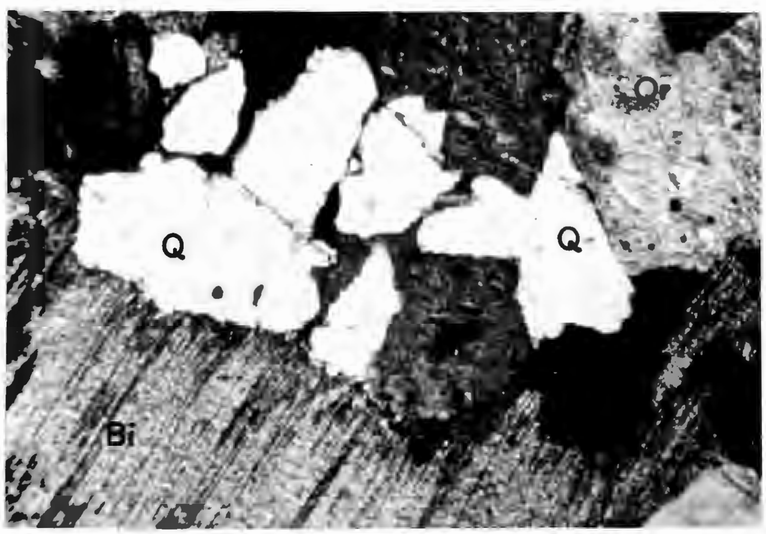


Figure 2. (x80) Biotite (Bi) with quartz (Q) and orthoclase-microperthite (Or) in Klondike granite. (x-nicols).

It has to be noted that zoning and zonal alteration of the plagioclase was observed only in two samples: in No. 24 a Klondike granite, and in No. 21 a Silvermine granite. Only the former showed the zonal, sericitic alteration. Twinning and zoning usually occurred together within the same crystal.

Emmons and Mann (1953) explain the petrogenetic importance of the type of zoning and twinning of the plagioclase. In short, the plagioclase feldspars formed from a true igneous liquid are, or have been oscillatorily zoned (compositional repetition within the crystal from calcic to sodic and back). On the other hand, if the plagioclase feldspars formed through recrystallization, without the benefit of a liquid, the zoning has been normal or progressive (compositional gradation from core to margin, which is usually from calcic to sodic). It has been recognized by the above authors that polysynthetic twinning develops late in the period of growth of the crystal. Also, the formation of such twinning usually eliminates the earlier zoning. They even go as far as to suggest that zoning is a prerequisite of twinning. The sodic plagioclase of granites generally exhibits a fine polysynthetic twinning, therefore it is quite possible that it has been zoned and has lost its zones through twinning.

The exact chemical determination of the composition of zones in samples Nos. 24 and 21 was not possible within the scope of this study; but in both cases, especially in that of sample No. 21, the zoning appeared between crossed nicols as successive bands of alternating extinction, and exhibited a fine texture. Thease features are characteristic of oscillatory zoning.

Quartz varies in amount from 20 to 40%. The least amount observed was in samples Nos. 24 and 40, the greatest in No. 37. It is always anhedral and often contains inclusions of feldspars and zircon.

Biotite and hornblende comprise the femic mineral suite. These make up from 2 to 8% of the rock. These minerals occur in the greatest amount in samples Nos. 24 and 40. Sample No. 37 contains the least of them. Biotite is more common and generally present. Some brown biotite was recognized, but more frequently it occurs as the green, pleochroic in yellowish green and dark green variety. A part of a large biotite grain with quartz and orthoclase-microperthite is shown in Plate 14, Figure 2. The biotite of the Klondike granite is often altered to chlorite. An interesting phenomenon was observed in sample No. 39, where chloritic and sericitic alteration of the same biotite grain took place side by side. Green hornblende is much more scarce than biotite, except in sample No. 24 where it exceeds in amount that of the biotite. Hornblende alters to chlorite and magnetite in some cases. Some pyroxene (pigeonite?) was observed in sample No. 38. The extinction angle of 38-44 degrees is noteworthy.

Zircon and apatite are the most abundant accessory minerals. Fluorite is also quite common. Primary magnetite is less abundant than the secondary alteration product. Sphene was observed only in sample No. 24. This marks its transition to the Silvermine granite for sphene is a characteristic member of the accessory mineral suite of this latter rock type. The occurrence of the accessory minerals in the Klondike granite is also very similar to that of the Doerun granite.

Silvermine granite

Geographic distribution. The Silvermine granite occupies the southern part of the main granite area. It forms a large continuous outcrop from Roselle southeastward to the St. Francois River in Madison County. Three isolated smaller outcrops occur a few miles east of the St. Francois River. The total outcrop area comprises about 15 square miles.

Megascopic features. The Silvermine granite is a medium to coarse-grained, light gray or pale pink rock, composed of orthoclase, plagioclase, quartz and femic minerals. Good outcrops occur in the vicinity of the St. Francois River in the SE 1/4 of section 12, T. 33 N., R. 5 E. Here large weathered boulders of the granite also occur on the river banks. These are similar to the "elephant rocks" at Graniteville, although on a much smaller scale (see Plate 15, Figure 1). Several aplitic dikes cut the granite. Some diabase is present among the boulders. One of these contains a coarse-grained inclusion of the Silvermine granite (see Plate 15, Figure 2).

Texture. The Silvermine granite has a holocrystalline, hypidiomorphic texture, which is mostly equigranular. Granophyric texture is absent.

Mineralogical composition. Orthoclase-microperthite comprises 40 to 50% of the Silvermine granite. The grains are euhedral to subhedral; Carlsbad twinning is often present. Inclusions of plagioclase, fluorite, apatite and magnetite are common. Some of the larger grains are completely altered to a sericitic-kaolinitic mass.

Plagioclase is next in importance and ranges from 30 to 40%. Its composition varies from Ab 86% to Ab 90%. Two generations of this mineral are present. Euhedral and subhedral grains can be observed in both. Some zoned plagioclase is present in sample No. 21 (see p. 39). Twinning is mostly according to the albite law, but some pericline twinning is visible. Minute inclusions are numerous. In samples Nos. 21 and 22 the amount of plagioclase almost equals that of the potash-feldspar. A small amount of microcline-microperthite was observed

PLATE 15. Megascopic appearance of the Silvermine granite.

Figure 1. Weathered boulders of the Silvermine granite along the St. Francois River, Madison County, Missouri.

Figure 2. Diabase boulder with inclusion of Silvermine granite along the St. Francois River, Madison County, Missouri.

in sample No. 23. The plagioclase shows more pronounced sericitic alteration than the potash-feldspar.

Quartz comprises about 20% of the rock. It is always anhedral and contains inclusions of feldspar and biotite.

Brown biotite and green hornblende comprise from 5 to 10% of the rock. The biotite is pleochroic in brown and green, usually subhedral and often is altered to chlorite and magnetite. The hornblende tends to be more euhedral than the biotite with some pseudo-hexagonal cross sections present. An interesting hornblende-sphene intergrowth occurred in sample No. 21. Slightly altered hornblende with quartz and orthoclase-microperthite is shown in Figure 1 of Plate 16. Hornblende with magnetite inclusions is shown in Figure 2 of Plate 16.

Sphene is the most abundant accessory mineral of the granite. It makes up 60% of the non-magnetic accessory mineral suite (Tolman and Koch, 1936). The sphene occurs in small, sharply defined grains, in a few cases exhibiting polysynthetic twinning. Other accessory minerals are apatite, fluorite, zircon, pyrite, and magnetite. Apatite occurs as long prismatic inclusions in feldspar, quartz and hornblende. Fluorite and zircon are less abundant. Some pyrite was observed in a few sections. In one case pyrite was oxidized to hematite and a few unreplaced parts of the pyrite are still visible. Magnetite occurs as both an accessory mineral and as alteration product of biotite.

PLATE 16. Hornblende in Silvermine granite.

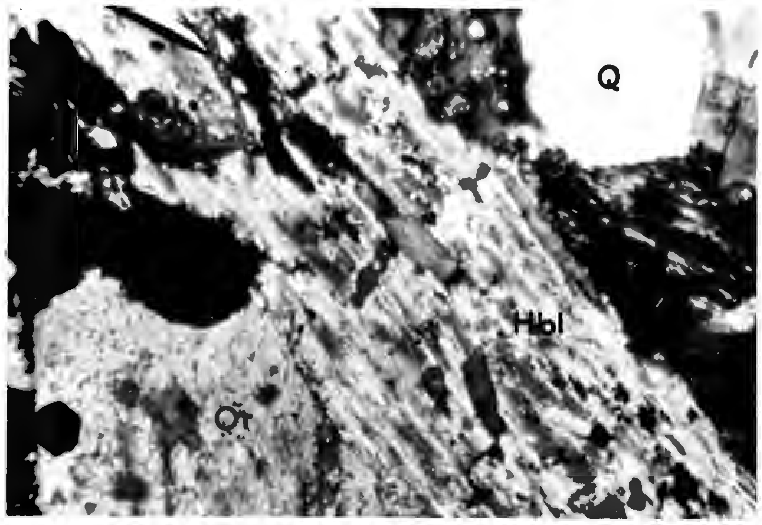


Figure 1. (x80) Hornblende (Hbl) with quartz (Q) and orthoclase-microperthite (Or) in Silvermine granite. (x-nicols).

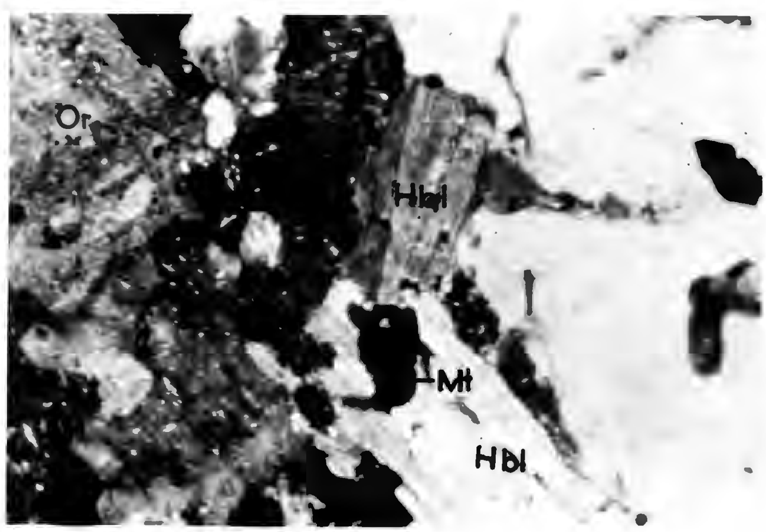


Figure 2. (x80) Hornblende (Hbl) with magnetite (Mt) inclusions in Silvermine granite. (x-nicols).

Various granite types

A brief description of various smaller, somewhat isolated granite outcrops examined by the writer is presented in this section.

Knoblick granite. The Knoblick granite crops out in the vicinity of Knoblick Mountain in St. Francois County, and comprises less than two square miles. The rock is dark brownish gray, medium to fine-grained and has a porphyritic appearance. Pale pink orthoclase and gray quartz phenocrysts up to 5 mm. in diameter are visible. Plagioclase is more abundant than in other granite types in the Southeastern Missouri area. It may make up 50% of the rock. The composition of the plagioclase varies from Ab 76% to Ab 80%. The amount of orthoclase-microperthite may range as low as 30%, while hornblende, biotite and some magnetite comprise from 10 to 15% of the rock. The accessory mineral suite includes zoisite, zircon, fluorite and sphene. In many respects this granite is similar to the Silvermine granite. Robertson (1949, p. 112) believes the two are genetically related. In view of the petrographic evidence, this is possible. The mineralogical composition of the two granite types are similar, if not identical. However, petrochemical data on this rock type shows a close relationship to the Fredericktown granite.

<u>Higdon granite.</u> The Higdon granite outcrops are located about 5 miles east of Fredericktown in Madison County. Five small and separate outcrops comprise approximately five square miles. The rock is distinctly red, fine-grained, composed almost entirely of orthoclase-microperthite and quartz. The little biotite present is mostly altered to chlorite. This rock resembles the Doerun granite in every respect and is thought to be closely related to that granite type.

<u>Ste. Genevieve granite.</u> The Ste. Genevieve granite crops out about ten miles northeast of Farmington in Ste. Genevieve County. The small outcrops comprise probably not over two square miles along Jonca Creek and the River Aux Vases. Two granite types are reported from this area (Weller and St. Clair, 1928). One type is reportedly related to the older granite stage, the other to the younger granite stage. Only the latter granite type was examined by the writer on the basis of one sample. A sample was collected in section 8, T. 36 N., R. 7 E., from the outcrops on the roadside. Orthoclase and quartz grains vary from one to two cm. in size. Orthoclase-microperthite comprises about 60%, quartz 30% and the femic minerals 10% of the rock. The latter is composed mainly of biotite, which is usually altered to chlorite.

<u>Viburnum granite.</u> The Viburnum granite is located a few miles northwest of Viburnum in Crawford County, where approximately three

square miles of the rock is exposed. The rock is distinctly red and medium-grained. It is composed of 50% orthoclase-microperthite, 5 to 15% plagioclase (Ab 90% to Ab 94%), 30 to 40% quartz and up to 5% femic minerals. The latter are brown pleochroic biotite and some hornblende. Some microcline-microperthite is also present. Magnetite, fluorite, and apatite comprise the accessory mineral suite. Granophyric intergrowth of quartz and orthoclase-microperthite is not uncommon (see Plate 16, Figure 1). The petrographic features of the Viburnum granite are quite similar to those of the Doerun granite.

Summary

The petrographic characteristics of the Precambrian granites of Southeastern Missouri are summarized in Table I. While a table of this type is somewhat generalized, it does, however, give a quick and easy comparison of the different granite types. Details are included under individual descriptions in the text.

Based on the modal mineral composition, each granite type was classified according to the Johannsen classification. The results are shown in the last two columns of Table I. Evidently the Johannsen classification does not give a sound basis for the differentiation of all of the granite types, as with the exception of the Knoblick granite, they can all be leucogranites.

PLATE 17. Granophyric texture of the Viburnum granite.

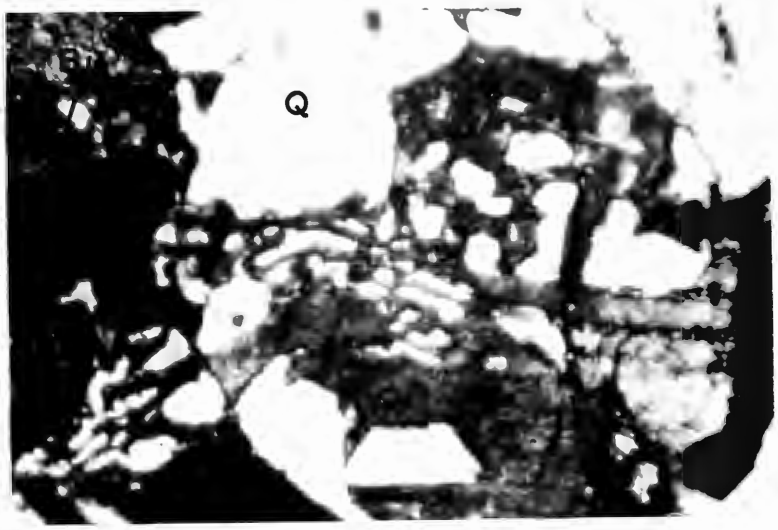


Figure 1. (x80) Granophyric intergrowth of quartz (Q) and orthoclase-microperthite (Or), biotite (Bi) on the left. (x-nicols).

Table I. Petrographic Characteristics and Johannsen Classification of the Granites of Southeastern Missouri.

Granite type		Color	Grain size	Texture: Equigranular	Texture: Porphyritic	Texture: Granophyric	Texture: Poikilitic	Essential minerals (%): Orthoclase-microperthite	Essential minerals (%): Microcline-microperthite	Essential minerals (%): Plagioclase (composition)	Essential minerals (%): Quartz	Essential minerals (%): Muscovite	Essential minerals (%): Biotite	Essential minerals (%): Hornblende	Essential minerals (%): Pyroxene	Accessory minerals: Fluorite	Accessory minerals: Apatite	Accessory minerals: Zircon	Accessory minerals: Sphene	Accessory minerals: Spinel	Accessory minerals: Magnetite	Accessory minerals: Hematite	Accessory minerals: Pyrite	Accessory minerals: Cassiterite	Accessory minerals: Molybdenite	Alteration minerals: Chlorite	Alteration minerals: Epidote	Alteration minerals: Magnetite	Alteration minerals: Hematite	Alteration minerals: Serpentine	Johannsen classification: Symbol	Johannsen classification: Name
Fredericktown		Purplish, dark red-brown	Fine grained (less than 1 mm).		x	x		35-60%		Ab 75-91 15%	25-35%			x 5-10%		x	x	x			x					x	x	x			126 226	Leucogranite Granite
Granite porphyries	Buford	Dark brown	Phenocrysts: 1-3 mm Groundmass: 0.1-1 mm		x	(x)*	x	x		x	x			x		x	x	x			x					x		x				
	Carvery Creek	Dark gray	Phenocrysts: 1-5 mm Groundmass: 0.5-1 mm		x	x		x		x	x			x		x	x				x					x		x				
Doerun Higdon Viburnum		Red	Fine to medium grained (1-10 mm).	x	(x)	x		55-60%		Ab 86-94 0-10% av. 5%	40-45%		x 3%			x		x			x					x	x	x		(x)	115 116 126	Kalialaskite Alaskite Leucogranite
Graniteville		Reddish	Medium to coarse grained (10-15 mm).	x	(x)			25-40%	20-50%	Ab 86-96 18-20%	25-35%	x	x 5-10%			x	x	x		x	x	?		x	x				x		116 126 216	Alaskite Leucogranite Sodaclase-granite
Klondike		Varies from pink to light gray	Medium grained (5-10 mm).	x		x		40-60%	2-5%	Ab 85-95 2-30% av. 15%	20-40%		x 2-8%	(x)	(x)	x	x	x			x					x			x		116 126	Alaskite Leucogranite
Silvermine		Light gray pale pink, usually darker than Klondike	Medium to coarse grained (5-12 mm).	x				40-50%		Ab 86-90 30-40%	20%		x 5-10%	x		x	x	x	x		x		x			x		x	x		126 226	Leucogranite Granite
Knoblick		Dark brownish gray	Medium to fine grained (0.5-5 mm)		x			30-45%		Ab 76-80 40-50%	10%		x 10-15%	x		(x)	x	x	x		x					x					226"	Adamellite

*Parentheses indicate less common occurrences.

PETROCHEMISTRY OF THE GRANITES OF SOUTHEASTERN MISSOURI

General Statement

Through the courtesy of the Missouri Geological Survey twenty-seven chemical analyses of the Precambrian granites of Southeastern Missouri were made available for petrochemical study. Though the localities of the individual samples are not identical with those selected for the petrographic and spectrochemical work (Figure 2), nevertheless the chemical samples are generally from the same area and each granite type is represented.

The granites of Southeastern Missouri have been classified by Forbes Robertson (1949) according to the C. I. P. W. classification. They belong to class I, where the sal:fem ratio is greater than 7.00 (persalic), and into orders 3 and 4 according to whether quartz is nearly equal to feldspar (quarfelic), or feldspar is dominant over quartz (quardofelic).

In the present study the system of Niggli (1954) was applied for petrochemical classification. Since the American reader may not be thoroughly familiar with this method, a brief explanation and a comparison is made with some of the better known systems of igneous rock classifications.

Petrochemical Classifications

In the classification of the rocks a distinction must be made between a mineralogical and a chemical classification. A mineralogical classification is based on the actual mineral composition of the natural rocks. A chemical classification is based on their chemical composition. This twofold classification arises from the fact that although a certain mineral assemblage uniquely determines the chemical composition of a rock, the opposite is not true. From a given chemical composition a variety of mineral assemblages might develop. Therefore the chemical systems are classifications of rock magmas rather than that of rocks, since from a given magma under different conditions entirely different rocks may crystallize. Besides the purpose of classification, petrochemical systems give information about the chemical history of rocks and their genetic relationships.

Quantitative chemical analyses of rocks are generally given in weight percentages of oxides. These include: SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O and MnO. In addition, other oxides important in certain rocks, such as TiO_2, CO_2, ZrO_2, P_2O_5, H_2O, etc., are often obtained. In the last few years, however, there has been an increasing tendency in the literature to use atomic or ionic percentages (Eskola, 1954).

Among the first petrochemists was Elie de Beaumont (Johannsen, 1939, p. 61). He attempted to establish the difference between the leucocrate and melanocrate rocks by mathematical means. From the weight percentages of the oxides of a chemical analysis he calculated the so-called "oxygen-ratios", which are based on the difference between the oxygen content of the basic oxides (Fe_2O_3, FeO, MgO, CaO) and the oxygen content of the silica. Elie de Beaumont then classified the rocks as acid, neutral or basic.

Loewinson-Lessing (Johannsen, 1939, pp. 63-65) was the first to use molecular numbers in the calculation. The weight percentages of the oxides were divided by their molecular weight. From these values he calculated the acidity coefficient of each rock (mols. of O in SiO_2 : mols. of O in the bases) and then divided them into four main groups: acid, neutral, basic and ultra-basic, depending on its value.

Michel-Levy and Osann (Johannsen, 1939, p. 70) further developed the method by distributing the components into groups. In the system of Osann group A contains the amount of alkalic feldspars $[(K, Li)_2O + Na_2O]$, group C the calcium feldspar (Al_2O_3 - A), and group F the "colored" or dark silicates [FeO + MgO + MnO + NiO + SrO + BaO + (CaO - C)]. The difficulty of this system was that Osann supposed that all the alumina enters the feldspars.

The leading idea of the American system of Cross, Iddings, Pirrson and Washington (1902) was to recalculate the rock analyses into a standard set of mineral molecules. The method offers a system according to which rock analyses can be quantitatively studied and compared from a petrological point of view. Molecular numbers are used for the calculation. The authors distinguish the actual mineralogical composition or mode from the calculated mineralogical composition or norm.

The distribution of the components into the standard normative minerals is performed in a prescribed sequence. The C. I. P. W. system is useful for genetic classification of rocks and for the calculation of the normative mineralogical composition. Unfortunately it does not account for the water content, and the calculation of such important rock-forming minerals as amphiboles and biotite is not possible. Also, the use of the molecular number is somewhat more inconvenient than that of the molecular norms.

The Niggli system (1954), which is a modification and simplification of the Osann system, applies the molecular norms for all purposes of petrochemical work. These are easier to work with due to the elimination of decimals. The following data and methods are used:

$$\text{Molecular norm} = \frac{\text{wt. \% of oxides}}{\text{mol. wt. of oxides}} \times 1000$$

Molecular norm = Molecular number x 1000

The molecular norms of the so-called basic oxides are summed up to 100, e.g.,

$$al + fm + c + alk = 100,$$

where al means the molecular norm of Al_2O_3,

fm means the molecular norm of FeO (all Fe as FeO) + MgO + MnO,

c means the molecular norm of CaO + (SrO + BaO, if any),

alk means the molecular norm of Na_2O + K_2O + (Li_2O + Rb_2O, if any).

These values recalculated to 100 are called Niggli or molecular values. In addition to these four, there are others. The value of si is the ratio of SiO_2 to the amount of the basic oxides:

$$si = \frac{SiO_2}{Al_2O_3 + FeO + MgO + CaO + Na_2O + K_2O} \times 100$$

The same factor which is used to make the molecular norms add up to 100 is applied individually to the molecular norms of all the rest of the oxides. Therefore:

ti = TiO_2; p = P_2O_5; h = H_2O; co_2 = CO_2; zr = ZrO_2; etc.

The value of mg refers to the ratio of MgO to fm, and that of k to the ratio of K_2O to all the alkalies (alk):

$$\underline{mg} = \frac{MgO}{FeO + MgO + MnO} \quad ; \quad \underline{k} = \frac{K_2O}{K_2O + Na_2O + Li_2O} \quad .$$

The latter values always lie between 0 and 1.

For the characterization of an igneous, metamorphic or sedimentary rock the following Niggli values are necessary:

si, al, fm, c, alk, ti, p, mg and k.

Examples of Niggli values of some rock forming minerals and the calculation of the Niggli values from the chemical analysis are given in Tables II and III.

The Niggli values permit:

1. Classification of rocks and interpretation of petrogenetic processes,

2. Calculation of the possible normative mineral composition of rocks.

Table II. Examples of the Niggli Values

of Some Rock Forming Minerals.

Mineral	Composition
Orthoclase	6 SiO_2 . 1 Al_2O_3 . 1 K_2O
Albite	6 SiO_2 . 1 Al_2O_3 . 1 Na_2O
Anorthite	2 SiO_2 . 1 Al_2O_3 . 1 CaO
Mg-Olivine	1 SiO_2 . 2 MgO

Mineral	Niggli Values						
	si	al	fm	c	alk	k	mg
Orthoclase	300	50	0	0	50	1	-
Albite	300	50	0	0	50	0	-
Anorthite	100	50	0	50	0	-	-
Mg-Olivine	50	0	100	0	0	-	1

Table III. Calculation of Niggli Values from Weight Percent of Oxides of a Rock Analysis.

27c*	wt. %	Mol. no. x1,000	si	al	fm	c	alk
SiO_2	77.85	1296	1296				
Al_2O_3	11.53	112		112			
Fe_2O_3	.71	4			4		
FeO	.58	7			7		
MnO	.00	0			0		
MgO	.09	2			2		
CaO	.73	12				12	
Na_2O	3.72	59					59
K_2O	4.19	44					44
H_2O	.34	11					
TiO_2	.14	1					
Total	99.88		1296	112	13	12	103

al (112)	=	46.6
fm (13)	=	5.4
c (12)	=	5.0
alk(103)	=	42.9
(240)		99.9

si(1296) = 540

k = 0.42
mg= 0.15

ti= 0.41

*Chemical analysis sample number.

Classification of the Southeastern Missouri Granites According to the Niggli Petrochemical Method

Niggli values were calculated for all the available chemical analyses of the Southeastern Missouri granites without further calculation of the normative mineral composition. A number of preliminary conclusions can be drawn from a mere inspection of these figures. Even without further calculation these values permit a fair estimation of the mineralogical composition. (Niggli, 1954, p. 16). Plotting the results is accomplished with the aid of diagrams. These, together with the QLM values which were calculated for classification purposes only, will be discussed in the following section.

Chemical character of the granites based on the Niggli values

si content. According to the si value magmas are generally divided into the following three groups:

si	> 200-225	acid
si	= 170-200	intermediate
si	< 170-130	basic

The si value of the granites of Southeastern Missouri ranges from 263 to 552. The majority of the samples has a si value above 400. Those with lower si values are mostly Fredericktown granites (but not necessarily all of them), the Silvermine granite (si = 350) and the Knoblick granite (si = 286). Despite this wide range of the si value, the rocks are all definitely acidic in their chemical character.

al : fm ratio. Further characterization of the magmas is based on the al : fm ratio. The value of fm for each rock is plotted against that of al as abscissa. The following magma types are distinguished:

al	=	fm	
+*		-	salic magmas
-		+	femic magmas
~		-	subfemic magmas
-		~	subalic magmas
-		-	subalfemic magmas
+		+	peralfemic magmas
+		~	semialic magmas
~		+	semifemic magmas

The header row reads "al = fm isofal".

Figure 3 shows the positions of the granites in this diagram. It is evident that most of the rocks lie in the salic field. The Doerun, Graniteville and Klondike granites are generally more salic, having

*The symbols mean: + = larger, - = smaller, ~ = nearly as much.

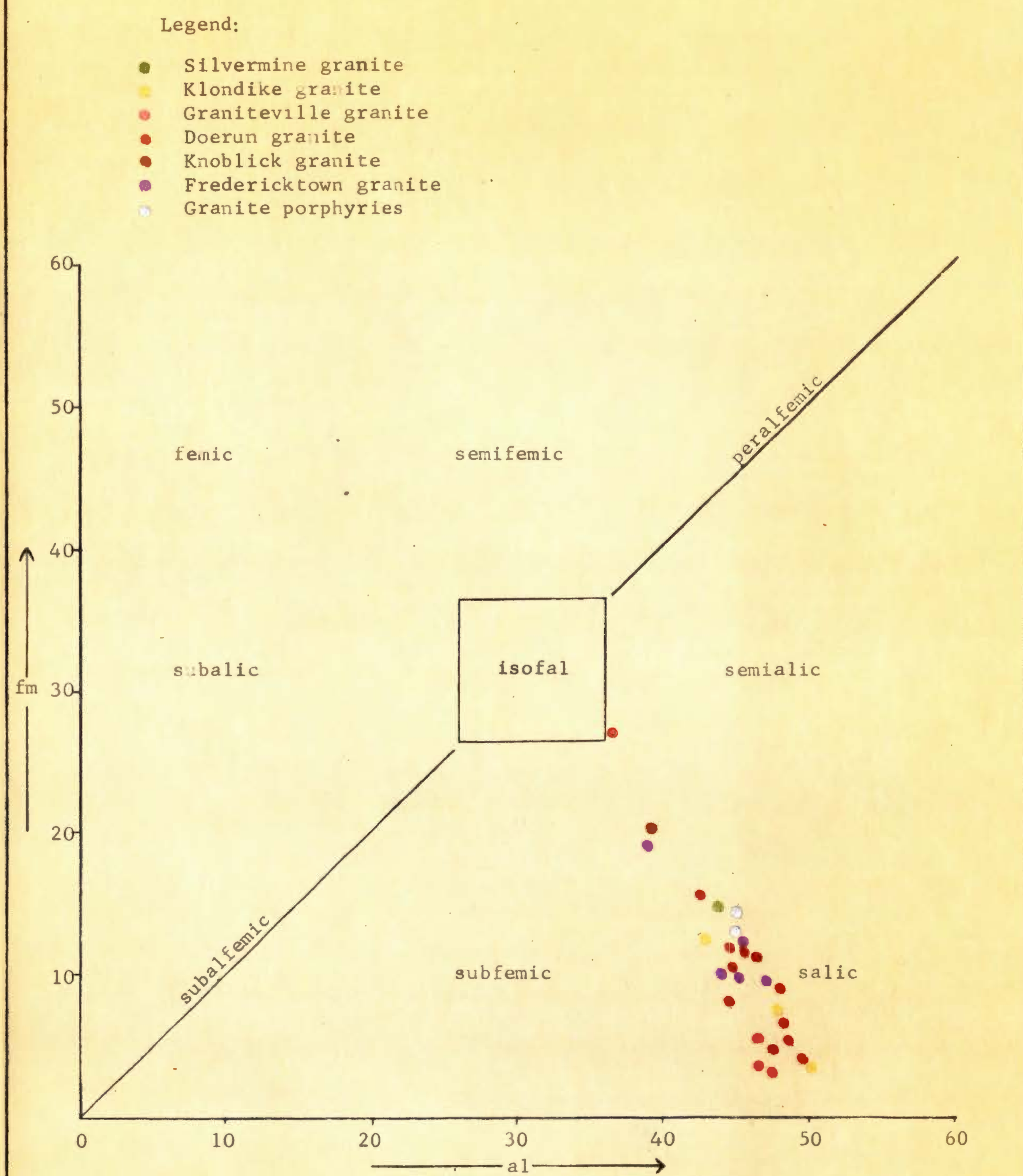


Figure 3. Chemical character of the granites of Southeastern Missouri, based on the al: fm ratios of Niggli.

their positions on the lowest part of the diagram. The Fredericktown granites, the granite porphyries and the Silvermine granite are higher in their fm-content, but they are still well within the salic field. The granite from Stono Mountain and the Knoblick granite are rather far away from the majority of the samples lying slightly in the subfemic field. This means a lower al and a somewhat higher fm value. But it does not mean that they are genetically unrelated to the other rocks since all the points are essentially in the same field on the graph, exhibiting a definite tendency toward the isofal field. Only sample No. 54c (reportedly a Doerun granite in contact with the Silvermine granite) is surprisingly out of the salic field, having a position at the corner of the isofal field.

al : alk ratio. A plot of the alk values against the al values as abscissa yields the results in Figure 4. The following fields are distinguished in the figure, each representing a magma type:

alk > al	peralkalic magmas
al > alk > 2/3 al	subperalkalic or relatively alkalirich magmas
2/3 al > alk > 1/2 al	intermediate alkalic magmas
alk < 1/2 al	subalkalic magmas

Note that in the plot the granites lie within the field of the relatively alkali rich magmas with the exception of the Knoblick granite.

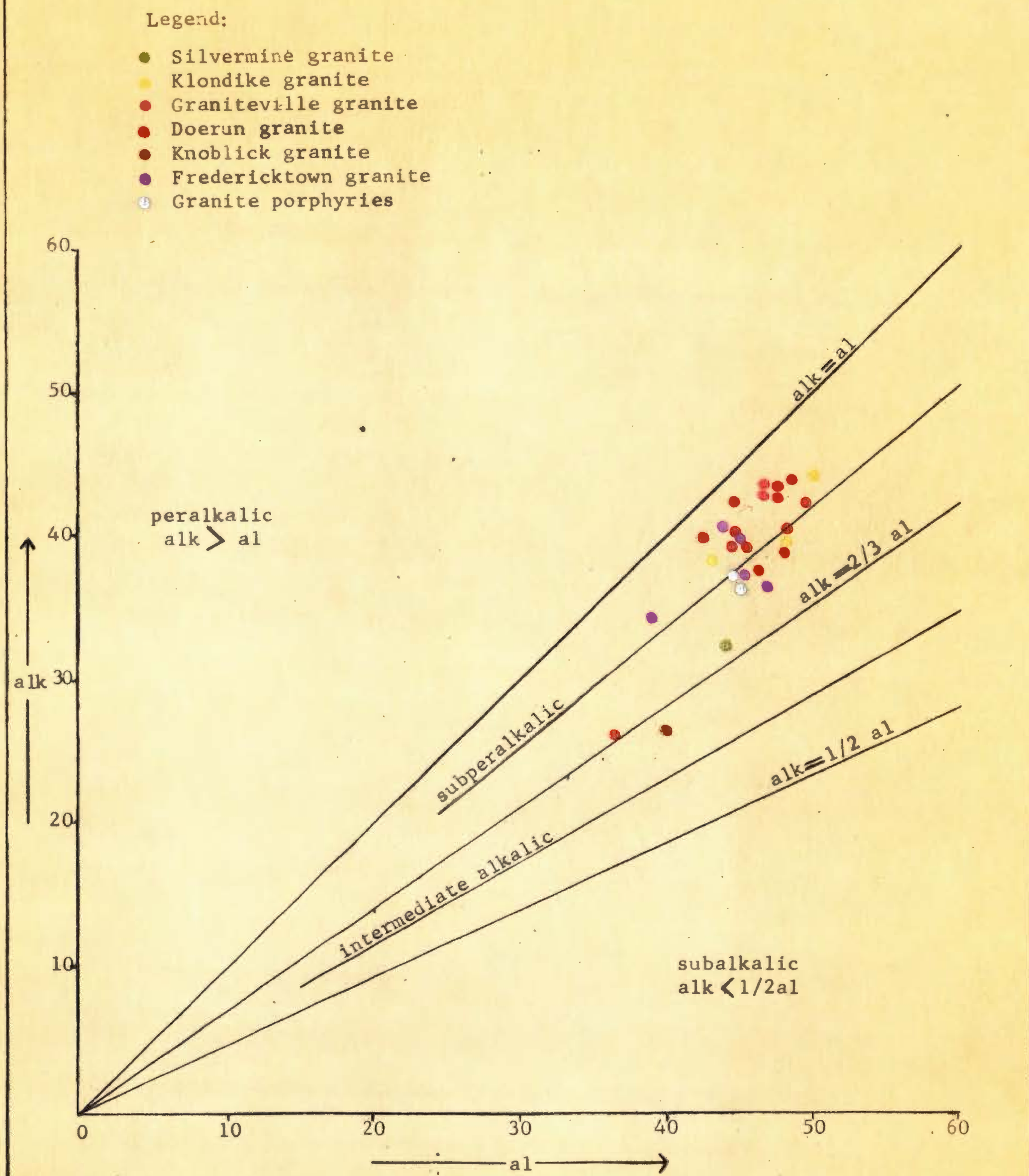


Figure 4. Chemical character of the granites of Southeastern Missouri, based on the al:alk ratios of Niggli.

which with a very low alk value is intermediate alkalic. The Doerun, Graniteville and Klondike granites have relatively higher alk values, while the Fredericktown granites, the granite porphyries and the Silvermine granite have lower alk values. Sample No. 54c again behaves very differently from the rest of the Doerun granites. With its very low alk value it therefore lies at the borderline between the relatively alkali rich and the intermediate alkalic fields.

c value. According to the c value the following magma types are distinguished.

$c > 25$	c-rich
$c = 15\text{-}25$	c-normal
$c < 15$	c-poor

All the granites have a c value of less than 15, therefore they have all originated from c-poor magmas.

The c value of the rocks ranges from 1.8 to 13.7. The highest c value was calculated for the Knoblick granite. The second highest c value is that of sample No. 54c ($c = 10$), but otherwise the Doerun, Graniteville and Klondike granites have somewhat lower c values than the Fredericktown granites, granite porphyries, and the Silvermine granite.

Summary. According to the Niggli values therefore the chemical character of the magma from which the granites have originated is acidic, salic, relatively alkali rich and c-poor. The rocks are definitely related to one another, but as the conditions of crystallization were different in each case the mineral character is not uniform for all the rock types. The Fredericktown granites and the granite porphyries, which are considered to be older, are generally less acidic, less salic, less alkalic and richer in c content than the younger rocks. The Knoblick granite behaves very similarly to the older granite series in its chemical character; therefore it is probably genetically related to those.

The variation diagram of the granites

The reduction of the twelve or more figures of a rock analysis to the five main values of si, al, fm, c and alk allows not only a better review of the chemical circumstances, but also a simpler graphic representation. The representation of five different values in a planar diagram presents difficulties, since the components of a single rock can not be plotted as a single point. The relationship of the values al, fm, c and alk to that of the si is such, however, that by the construction of a variation diagram the problem is easily solved.

Of the five values si exhibits the widest range of variation. In the granites of Southeastern Missouri they range from 263 to 552. The other four values vary within much smaller limits. Moreover, al, fm, c, and alk, are all dependent on the amount of SiO_2 in the rock. With lower si values the amounts of al and alk are generally lower, but at the same time the corresponding fm and c are higher (in accordance with the rule: al + fm + c + alk = 100). With increasing si values the amount of al and alk increases, that of fm and c decreases.

With this consideration the variation diagram is constructed so that the values of al, fm, c and alk are plotted on the ordinate against the value of si on the abscissa. Each rock will be represented by its si value and above it on a vertical line the corresponding al, fm, c and alk values are plotted, using a different symbol for each. When all the analyses with their varying si values are plotted on the graph, the corresponding symbols for the four others are connected. The result is a diagram with four curves as shown in Figure 5. The al and alk curves have an upward tendency to the right (increasing si, increasing al, alk), the al values remaining always higher than those of alk. The c and fm curves tend downward to the right (increasing si, decreasing fm, c), the fm values being generally higher than those of c. The different analyses are represented by their numbers above the corresponding si positions.

A complete variation diagram contains rock analyses with a much wider range of si, from 50 upwards to about 500. Such a diagram exhibits the variation of the Niggli values in the whole series of magmatic

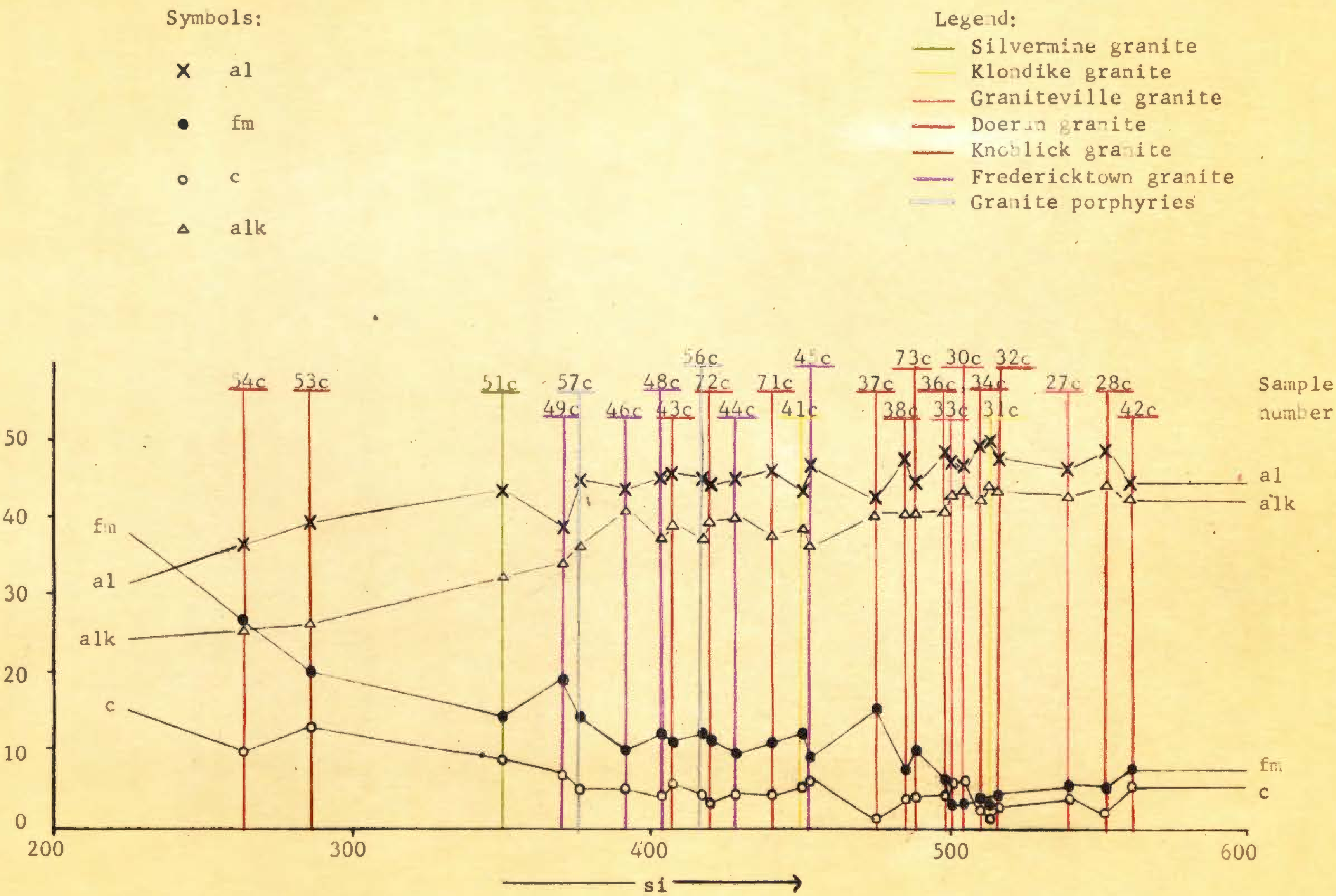


Figure 5. The variation diagram of the granites of Southeastern Missouri.

differentiation. As such, it is characteristic of the magmatic province in which the rocks belong. Since the analyzed granites were all rather strongly acidic, the diagram of Figure 5 should be regarded as the right half of a complete variation diagram. Note that si values below 200 are not represented, since such low values were not encountered for these rocks. If the andesites, basalts, diabases, etc. of the Southeastern Missouri Precambrian were plotted on this variation diagram, with their lower si values, we would have the complete variation diagram for this particular rock province. With such an addition the al and alk curves would continue to decline to the left, the fm and c curves would rise in that direction. At a certain point an intersection of the alk and c curves would occur, as in the intersection of curves al and fm shown in Figure 5. These intersections on the variation diagram are important in the recognition of the petrographic province, the corresponding si values being determinative.

A petrographic province as defined by Turner and Verhoogen (1951, p. 66) is a "broad region over which presumably related igneous rocks have been injected or poured out during the same general epoch of igneous activity." Members of a petrographic province may be relatively uniform in composition, but more usually they are varied both in mineralogy and in chemical composition. There may be a wide range of chemical variation in the series as a whole, but the chemical characters of the representative rocks tend to vary regularly. Some igneous provinces, for example, are characterized by a high soda content in all members.

Many petrographic provinces have been described, some of them in great detail (Burri and Niggli, 1945). It is interesting to note that even on a world wide basis they tend to conform to one of the relatively small number of standard types. Generally, rock suites intruded into fold mountains of orogenic regions are calcic, while those associated with vertical faulting in non-orogenic areas are alkalic. As the former rock types were observed in the folded mountains of the circum-Pacific orogeny, this rock suite was called Pacific (Barth, 1952, p. 169). Similarly, as the alkaline rock series was associated with the coastal districts and islands of the non-orogenic Atlantic basin, it was called Atlantic. These geographical adjectives were rather unfortunate, however, for both "Pacific" and "Atlantic" rock suites were described outside these general geographic areas. Therefore it is better to describe the provinces according to their chemical character, that is calcic for Pacific and alkalic for Atlantic. There is, however, no unanimity in the usage of terms. Certain transitions also exist between the two main petrographic provinces. Peacock (Barth, 1952, p. 172) proposed a fourfold classification and divided the Pacific province into calcic and calc-alkalic, and the Atlantic province into alkali-calcic and alkalic, thus providing for such transitions.

All these factors should be borne in mind when Niggli's classification is presented in this study. Niggli's Pacific province includes the calcic and calc-alkalic province of Peacock. He divided the alkalic province into two: the Atlantic and the Mediterran, according to w hether sodium or potassium are dominant, respectively. Barth (1952, p. 172) gives a good comparison of the different connotations.

It is possible to determine exactly the degree of alkalinity of a rock series on the variation diagram with the aid of the alkali-lime index. It was originally proposed by Peacock (Barth, 1952, p. 172) and Niggli adopted the idea for his system. The value of the abscissa of the point of intersection of the $\underline{alk}$ and $\underline{c}$ curves expressed in terms of $\underline{si}$ is the alkali-lime index. The smaller the index is, the more alkalic the rock suite is, and the higher the index is, the more calcic the rock suite is. Specifically speaking, if the alkali-lime index is at $\underline{si} = 175$ or more, the rocks belong to Niggli's Pacific (calcic) province; if it is less than 175, they are either Atlantic or Mediterran (alkalic).

Figure 5 does not show the alkali-lime index of the granites. It can not be constructed from actual points because the number of analyses in the lower $\underline{si}$ region was very few. We have also mentioned that Figure 5 represents only the right hand side of a complete variation diagram of the Precambrian igneous rock series of Southeastern Missouri. But from the general trend of the two respective curves, it seems that the intersection would occur above 175 if more analyses were plotted on the diagram.

There are other factors which determine the petrographic province. According to the one mentioned above and the QLM triangle (see next section) it is very probable that the granites belong to the Pacific province. If so, however, they are not typical members of this province. The very high alkali content of the rocks and the astonishingly low c values are not typical of Niggli's Pacific or the calcic province. On the other hand, rocks of the alkalic (Atlantic and Mediterran) provinces seldom reach such high si values as these granites. If not of the Pacific type, of the latter two alkalic provinces they could only belong to the Mediterran (high-potash) province, as their sodium content is generally smaller than that of rocks of the Atlantic (high-soda) province. The Atlantic province is soda-high, with k values not exceeding 0.3. Considering this, the possibility of these rocks belonging to the Atlantic petrographic province of Niggli is definitely excluded.

The k value expresses the ratio of potash to all the alkalies. Therefore higher k value means a more potash-rich rock. Figure 6 shows the relationship between the values k and mg (ratio of MgO to all

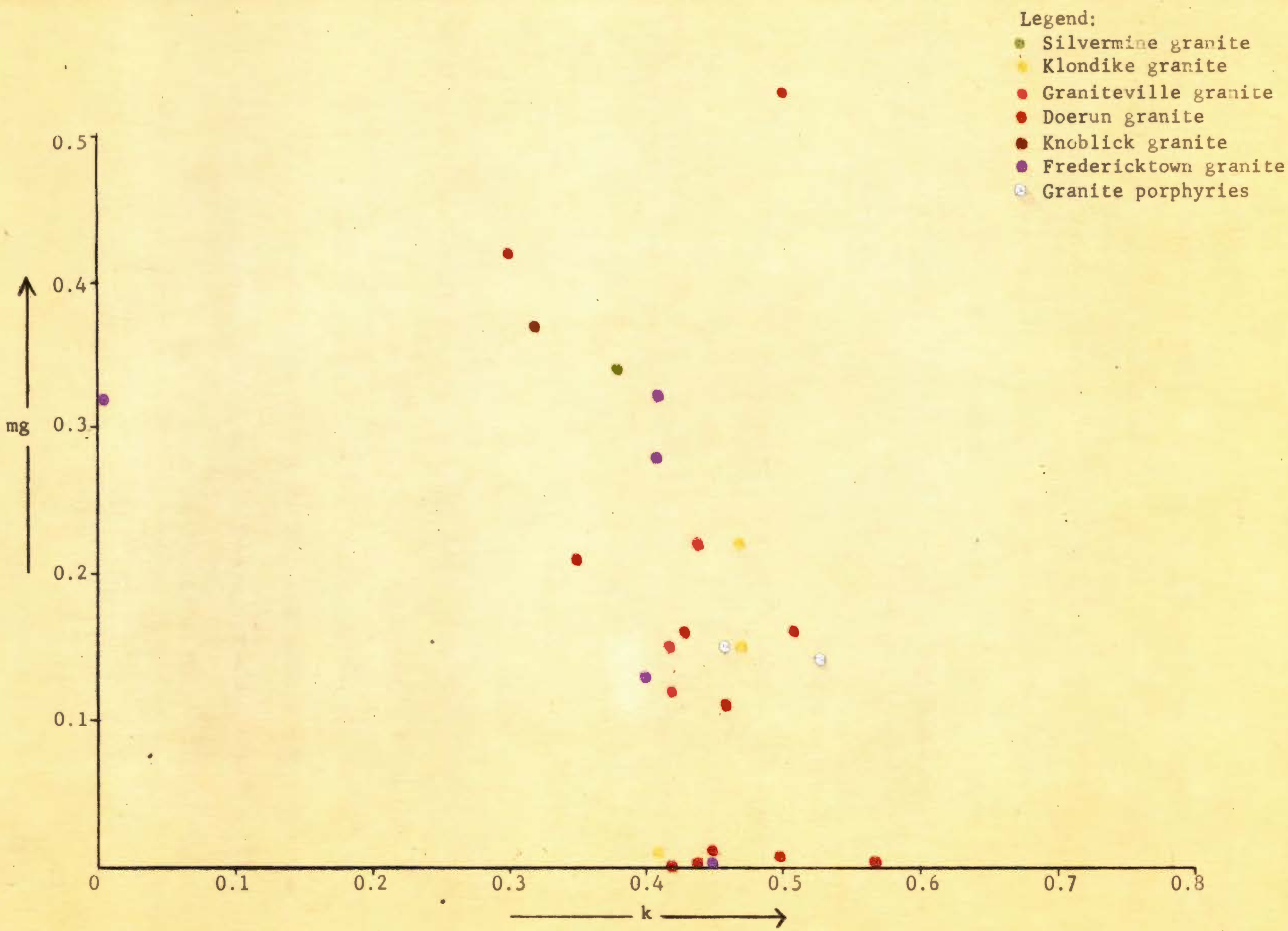


Figure 6. Chemical character of the granites of Southeastern Missouri, based on the k:mg ratios of Niggli.

the ferromagnesian compounds). The majority of the analyses has k values between 0.4 and 0.5. Rocks of the Pacific province (if they are acidic enough) may generally attain such values. And even in this province c can be as low as 3.5. Therefore the writer concludes that the granites are essentially Pacific in character, but show a certain tendency toward the Mediterran province. If Peacock's terminology were used, they could be classified as calc-alkalic.

According to Niggli, the k-mg diagram may also be characteristic of the petrographic province, although it can not be regarded as certain evidence. In the Pacific province type for high si the k values are higher, and the mg values are smaller. This is approximately so in Figure 6.

More interesting is the position of the different granite types on this diagram. The highly siliceous Doerun, Graniteville and Klondike granite types have higher k and lower mg values, while the Fredericktown granite types are a little poorer in k, richer in mg, and the Silvermine granite has definitely lower k value, slightly more mg. Sample No. 54c behaves in an unusual manner again, and with such low k and high mg values it cannot possibly be a typical Doerun granite. Sample No. 46c (a Fredericktown granite) has the smallest k value, as in this analysis the weight percent of Na_2O was 7.85, while that of K_2O only 0.19.

This must either be a special rock type or analytical error. Sample No. 37c from Bismarck has a very high <u>mg</u> value, (0.53), but it is just as rich in <u>k</u>.

<u>The QLM triangle</u>

As we have seen the graphic representation of chemical analyses of rocks is not possible on the variation diagram by a single point. For several reasons, however, such a representation would often be more convenient. If one applies a simple calculation to the Niggli values, the purpose can be achieved in a triangular diagram. For the rules of computing the three base groups Q, L, and M from <u>si</u>, <u>al</u>, <u>fm</u>, <u>c</u> and <u>alk</u> the reader is referred to Burri and Niggli (1945, pp. 95-97).

The letter Q stands for quartz, it is located at the apex of the triangle. The right lower corner is L for the leucocrate base group. The mineral molecules kaliophilite, nepheline and calcium aluminate are located at L. They are characteristic constituents of the light colored feldspar minerals. On the QL side of the triangle at about Q = 40 is the position of the feldspars (F), orthoclase, albite, anorthite. The left lower corner M is assigned to calcium orthosilicate, forsterite and fayalite, which because of their participation in dark minerals, are called melanocrate base groups. On the QM side of the triangle at about

Q = 25 are located the pyroxenes (P). The amphiboles and biotites are within the triangle, their positions being determined by the Q : L : M ratio in them.

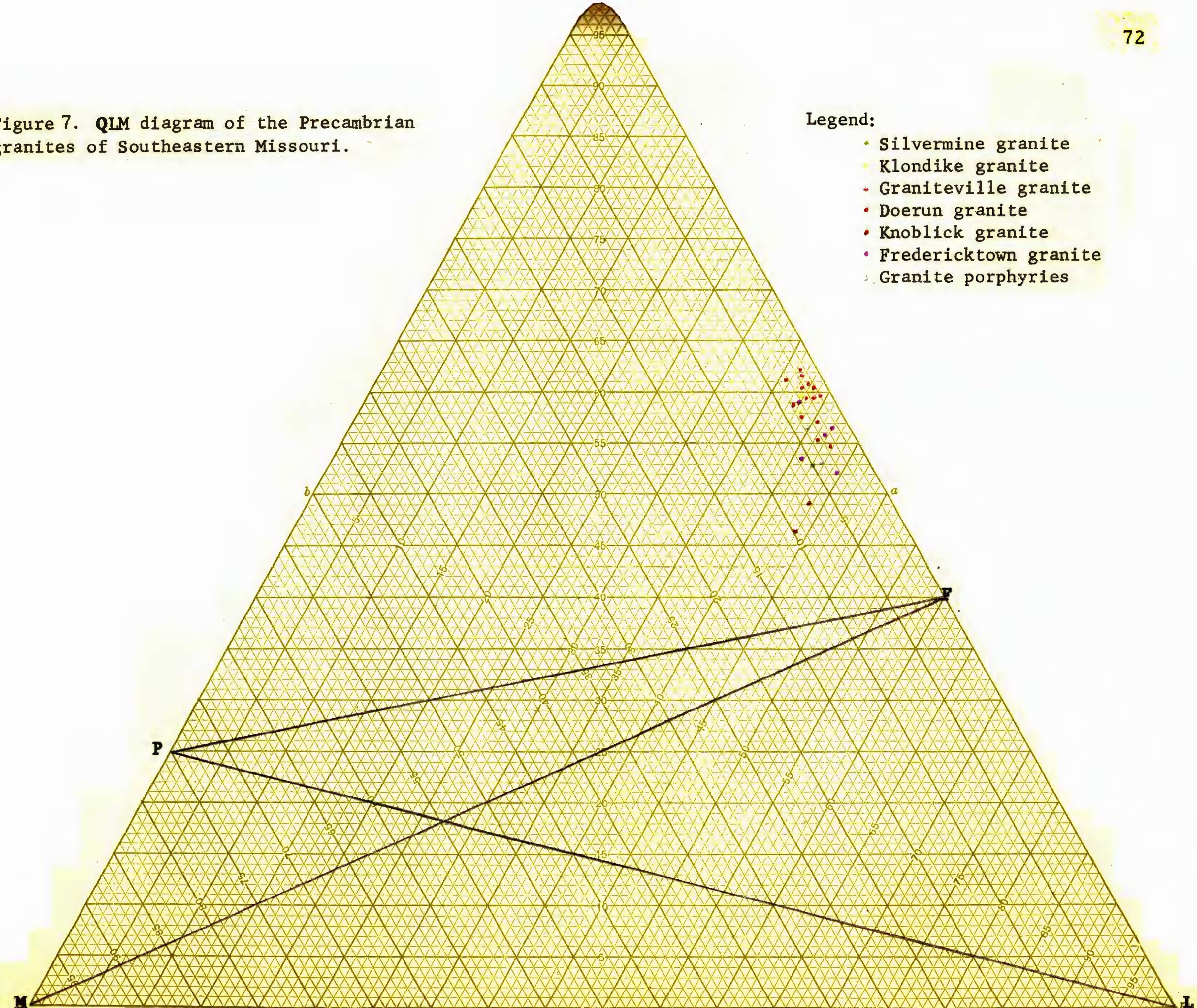
A rock analysis can also be expressed in terms of Q, L, and M so that Q + L + M will always be 100 (Q, L, and M then will mean percentages). Then one point in the triangle is representative of one particular rock analysis. In this way a large number of rocks can be compared with practically a glance at the diagram. But what is even more important, the three petrographic provinces of Niggli can easily be recognized on a QLM triangle.

Figure 7 is a QLM diagram with the granite analyses plotted on it. As before, the difference between the rock types is well seen. The Doerun, Graniteville and Klondike granites are higher up in the triangle, most of them with Q values above 57%. The Fredericktown granites, the granite porphyries and the Silvermine granite are located below this first group, with Q values between 52% and 57%. The Knob-lick granite has only 49% Q and much more M than any of the others, except Sample No. 54c, which with its lowest Q and highest M value is the most basic of all the analyses.

It should be noted again that a complete series of magmatic differentiates would occupy positions in such a way that the points of the more basic members would always have lower Q and higher M values.

Figure 7. QLM diagram of the Precambrian granites of Southeastern Missouri.

Legend:
- Silvermine granite
- Klondike granite
- Graniteville granite
- Doerun granite
- Knoblick granite
- Fredericktown granite
- Granite porphyries



It would be the continuation of the granite field in a southwesterly direction. Such a position of rocks in the QLM triangle is typical of the Pacific petrographic province. Therefore it seems positive, together with the evidence obtained in the previous section, that the granites belong to the Pacific province of Niggli (or the calc-alkalic province of Peacock), with a somewhat higher alkali content and a lower c content, than typical representatives of this province.

Magma types

The granites can best be classified according to their mineralogical composition (Johannsen classification) and the chemistry of the magmas out of which they have been formed (magma type). As each petrographic province has different magma types, it first had to be ascertained to which province the granites belong. This problem was discussed in detail in the foregoing section and the granites were all classified as essentially Pacific in character.

The magmas of the Pacific province were further classified according to the Niggli values (si content, al : fm ratio, al : alk ratio and c value). The chemical character of the granite magmas was described on page 61.

With these considerations in mind the Niggli values of each granite analysis were then compared with the Niggli values of each specific magma type listed by Burri and Niggli (1945, p. 51, Table 1). The magma type of the granite is that one which most closely approximates a described type in the Burri and Niggli grouping. The Niggli-QLM-values, and the magma types of the analyzed granites of Southeastern Missouri are listed in Table IV.

Those rocks which are of the same magma type suggest a close genetic relationship. Thus the Doerun, Graniteville and Klondike granites, each in the aplitgranitic magma type, suggest that they all have crystallized from essentially the same magma, which was aplitgranitic in character. Differences in the appearance and mineralogical composition of these rocks might have been caused by relatively minor local variations in the physico-chemical conditions during crystallization.

The problem of the Fredericktown granites can not be solved so easily. Samples Nos. 44c and 45c have aplitgranitic magmas, while samples Nos. 48c and 49c, and both the granite porphyries have engadinitgranitic magma type (less acidic, less salic, less alkalic, more femic and more calcic than the aplitgranitic). They are both essentially leucogranitic magmas. Sample No. 46 with its high sodium content was found to be natronengadinitic, which is a trondhjemitic magma. If the Fredericktown granites and the granite porphyries are members of an older intrusion, the nature of that magma was probably very similar to the younger magma type which produced the Doerun, Granite-

Table IV. Niggli-, QLM-values and Magma Types of the Granites of Southeastern Missouri.

Granite type	No.	Q	L	M	si	al	fm	c	alk	k	mg	ti	p	Magma type
Graniteville	27c	61.8	36.8	1.4	540	46.6	5.4	5.0	42.9	.42	.15	.41	.00	Aplitgranitic
Doerun	28c	62.1	36.2	1.5	552	48.7	5.1	2.1	44.0	.43	.16	.00	.00	Aplitgranitic
Graniteville	30c	59.6	38.9	1.3	503	46.8	3.5	6.2	43.3	.44	.22	.00	.00	Aplitgranitic
Klondike	31c	60.0	38.3	1.5	514	50.0	3.6	2.0	44.3	.47	.22	.00	.00	Aplitgranitic
Doerun	32c	60.2	38.5	1.1	516	47.7	4.8	3.6	43.7	.51	.16	.40	.00	Aplitgranitic
Graniteville	33c	59.6	39.3	1.0	500	47.6	3.1	6.2	42.9	.42	.12	.00	.00	Aplitgranitic
Higdon	34c	60.6	37.7	1.6	512	49.7	4.0	3.6	42.5	.44	.00	.40	.00	Aplitgranitic
Doerun	35c	61.3	35.6	3.2	500	48.2	9.1	3.5	39.1	.35	.21	.39	.00	Aplitgranitic
Doerun	36c	60.3	37.4	2.1	498	48.2	6.7	4.3	40.7	.46	.11	.39	.00	Aplitgranitic
Bismarck (Doerun)	37c	58.9	37.3	3.7	476	42.4	15.5	1.8	40.1	.50	.53	.75	.00	Aplitgranitic
Klondike	38c	59.8	37.6	2.5	485	47.8	7.7	4.2	40.1	.47	.15	.38	.00	Aplitgranitic
Klondike	41c	58.1	38.6	3.2	452	43.2	12.4	5.8	38.4	.41	.08	2.20	.00	Aplitgranitic
Undifferentiated (Doerun?)	42c	57.3	40.1	2.5	461	44.5	7.9	5.3	42.2	.45	.09	2.64	.00	Aplitgranitic
Ste. Genevieve	43c	54.7	42.8	2.3	407	45.7	11.7	6.0	39.3	.46	.34	.63	.00	Engadinitgranitic
Fredericktown	44c	55.9	41.5	2.5	428	45.0	9.9	4.9	40.0	.41	.28	1.77	.00	Aplitgranitic
Fredericktown	45c	59.1	37.8	3.1	453	46.9	3.4	6.7	36.8	.45	.00	1.87	.37	Aplitgranitic
Fredericktown	46c	52.6	44.1	3.2	391	43.8	10.1	5.2	40.9	.01	.32	2.27	.32	Natronengadinitic
Fredericktown	48c	56.6	41.9	1.3	403	45.3	12.4	4.7	37.5	.40	.13	.67	.33	Engadinitgranitic
Fredericktown	49c	53.4	40.4	6.1	371	38.9	19.3	7.2	34.4	.41	.32	1.80	.31	Engadinitgranitic
Silvermine	51c	53.0	41.9	4.9	350	43.8	14.8	9.0	32.3	.38	.34	1.40	.00	Yosemititgranitic
Knoblick	53c	49.2	43.6	7.1	286	39.3	20.4	13.7	26.4	.32	.37	1.20	.25	Granodioritic
Doerun & Silvermine contact	54c	46.3	43.8	9.8	263	36.6	27.1	10.0	26.1	.30	.42	1.20	.48	Granitic
Granite porphyry	56c	56.3	39.9	3.7	420	45.1	12.2	4.8	37.7	.53	.14	1.30	.00	Engadinitgranitic
Granite porphyry	57c	53.3	42.2	4.4	376	44.9	14.5	5.1	36.7	.46	.15	1.50	.00	Engadinitgranitic
Doerun	71c	57.8	38.5	3.7	441	46.3	11.3	4.4	37.9	.57	.00	.72	.00	Aplitgranitic
Doerun	72c	55.5	41.2	3.3	420	44.5	11.9	3.8	39.6	.50	.05	.70	.00	Aplitgranitic
Doerun	73c	59.6	37.9	2.3	489	44.7	10.1	4.3	40.7	.42	.00	.78	.39	Aplitgranitic

ville and Klondike granites. Yet physico-chemical conditions must have acted quite strongly to produce the three different magma types observed in these rocks. Based on petrochemical evidence only, it is also possible that there was only one intrusion, essentially an aplitgranitic one, which had an aureole of a more basic and varied character. The products of this aureole would be the Fredericktown granites and the granite porphyries. The granite from Ste. Genevieve County (sample No. 43c) is also engadinitgranitic and this suggests its relationship to the Fredericktown granites.

The Knoblick granite has a granodioritic magma type, which is less acidic and less alkalic than the leucogranitic magmas. As in other chemical aspects, this analysis was very similar to the Fredericktown granites, this rock is thought to have been formed under conditions similar to the Fredericktown granites.

Data for the Silvermine granite are very inadequate. Only one analysis was available and this suggests that the Silvermine granite was of a yosemititgranitic magma type. This one analysis, however, is not enough to permit a definite conclusion, but according to the geologic and petrographic evidences it is probably correct to assume that this is a different granite. The anomalous behavior of sample No. 54c is probably the result of its being a contact product between the Silvermine and Doerun granites.

Summary on Petrochemistry

The Niggli petrochemical classification of twenty-seven chemical analyses of Precambrian granitic rocks from Southeastern Missouri revealed their petrogenetic relationships. The chemical character of the magma out of which they have formed was acidic, salic, relatively alkali rich, and lime poor. The Doerun, Graniteville and Klondike granites are in the aplitgranitic, the Fredericktown granites and granite porphyries in the aplitgranitic and engadinitgranitic, the Knoblick granite in the granodioritic, and the Silvermine granite in the yosemititgranitic magma type. All the rocks belong to the calc-alkalic petrographic province.

SPECTROGRAPHIC ANALYSIS OF THE GRANITIC ROCKS OF SOUTHEASTERN MISSOURI

General Statement

Detailed spectrographic analyses of the Southeastern Missouri Precambrian igneous rocks have not been published. Available chemical analyses report only the more abundant elements. The latter are important in determining the nature and chemistry of the original magma and serve as a basis for classification. Spectrochemical analyses, however, yield data on the less abundant trace elements. This technique has not been extensively applied in rock analyses, although it offers useful results.

Bray's (1942) investigations on the distribution of minor elements in igneous rocks from Jamestown, Colorado, allowed him to draw some interesting conclusions. Acidic igneous rocks of both Precambrian and Tertiary age were analyzed. The results indicated that the minor elements were systematically distributed in the rocks and their distribution permitted identification of any rock in the district.

The analysis of New England granites by Shimer (1943) showed that each granite type had well marked minor element characteristics whereby it could be distinguished from the others. He also established a relationship between grain size and minor element content of the granites, noting that the finer the grain of the granites, the more abundant the minor elements.

In the present investigation forty-four samples of the Precambrian granites of Southeastern Missouri were analyzed spectrographically. Since several distinct types of granitic rocks are known in this area, the question arose as to whether these rocks differ in their trace element content. An attempt was made to recognize the distribution pattern of the minor elements in the rocks and, if possible, set up a scheme by which the rocks could be identified on this basis. Since previous data were not available, comparisons were not possible. However, comparisons with analyses of similar rocks from other districts were made.

This trace element study may serve as an initial step in the investigation of the Precambrian igneous rock types of Southeastern Missouri on a spectrographic analysis basis. Much more detailed research is necessary, however, before the final answers can be given.

Preparation of Samples

In the collection of various rock samples (see page 10) special attention was given to obtaining fresh material. The samples were collected from the best rock exposures which showed the least weathering. In order to prevent contamination the labeled samples were placed in clean paper bags. The geographic location of each sample is shown by a dot on Figure 2. The corresponding numbers are indicated on overlay No. 1 of Figure 2.

The samples selected for the qualitative spectrographic analysis were large. Most of these weighed about one pound each. Only ten samples were smaller, the smallest, a contributed sample from Knoblick, weighed about one ounce. The samples were carefully cleaned and later crushed in a jaw crusher of the Missouri Geological Survey. The jaws are made of cast iron. The trace element composition is not available, but is not considered important because of the sampling procedure used. After each sample was crushed the equipment was then cleaned with a brush.

The sizing of the material consisted of two stages: 1) the sample was crushed to a minus half inch, 2) then it was pulverized in a pulverizer with cast iron plates (composition not available) to a fine powder of minus 100 mesh. The powder was placed in clean glass containers and then thoroughly mixed on glazed paper. A small portion of this powdered and mixed sample was placed in clean paper bags.

Analytical Methods

The instrument

The Missouri Geological Survey 3 meter, 15,000 line per inch, grating spectrograph made by Baird Associates (1951) was used for the spectrographic analyses. The total number of grating rulings was 55,000. The useful wavelength range of the instrument ranged from 1800 A to 5250 A. The dispersion at the setting used was 5.5 A/mm over the entire plate for the first order. The theoretical resolving power of the instrument is 55,000.

Operating technique

The essense of spectrographic analysis is the vaporization of the sample and the recording of the light emitted. The vaporization of the samples takes place on the optical bench part of the instrument where the sample is placed in graphite electrodes. A high temperature arc is produced through the electric power unit.

This investigation dealt with the analyses of complex materials of high melting points. Each sample contained a large number of elements. In order to excite all the possible components very high temperatures were required. These were obtained by the use of the cathode layer method of carbon arc spectral analysis. Here a D.C. arc is produced in such a manner that the lower electrode containing the sample is always the cathode. Only the light near the cathode passes into the spectrograph. The temperature of such an arc ranges to 3000 degrees Celsius. The D.C. arc was operated at 10 Amperes and 35-45 Volts.

A small amount--about 0.2 gram--of each sample was taken from the paper bags and dampened with a special mixture of collodion and anisole. This made the mounting easier and since they are both organic materials there was no danger of introducing alien elements in the sample. The samples then were mounted in pure graphite electrodes. The composition of the electrodes was available. They contained iron, magnesium, manganese and sodium as impurities.

The mounting of a spectrograph in general and the Eagle mounting used by the Baird instruments are illustrated in Figure 8. The arc radiation is directed into the spectrographic system through a lens and then through a slit (S). The slit width was adjusted to 25 microns. The light passes to the concave grating (G) where by diffraction the spectrum is produced and reflected to the photographic plate (A and E in the upper diagram, P in the lower diagram). Since no two elements produce the same spectrum, a complete record of the light radiation, and therefore of the elements present, is made.

The recording of the spectra was done on Spectrum Analysis No. 1 emulsion on 4" by 10" plates. These plates were developed in D-19 solution for 3 minutes. Each sample was exposed three times. First for half a minute, then for one and two minutes, respectively.

For the majority of the elements present, the wavelength range was selected between 2460 and 3875 A. For Ba and Sr a different range was required since the most sensitive lines of these elements lie above 4000 A. Separate analyses were run on these two elements in the range

A. Rowland circle diagram for grating spectrograph.

B. Relation of the Rowland circle to modified Eagle mounting used in Baird Associates Grating Spectrographs.

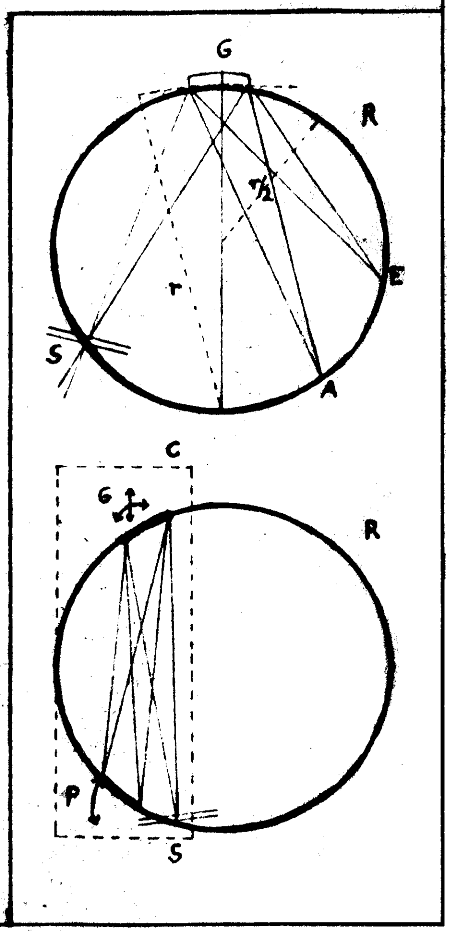


Figure 8.

The Eagle mounting.

(After Baird Associates, Bull. 32.)

between 3640 and 5050 A. This time only two exposures were made, one for a minute, the other for two minutes.

The plates were analyzed by Miss Mabel E. Phillips of the Missouri Geological Survey on a Jarrel & Ash type comparator-densitometer.

Qualitative Analysis

The present study was restricted to qualitative analysis, though a semi-quantitative aspect was used. Instead of merely noting the presence or absence of an element, an estimate was made of the relative density of the element line when compared with the same line in other spectra on the same plate. Since the density of a line is a function of the amount of the element present, one can tell that sample 1, for instance, has more of a certain element than sample 2, and less than sample 3. Of course this gives no indication as to absolute quantities. This semi-quantitative approach was especially helpful in analyzing the trace element content of the rocks.

To facilitate the work an arbitrary scale was set up to indicate relative quantities of the elements. The scale is as follows:

H - High, major constituent

P - Present, intermediate quantity

L - Low, minor constituent

VL - Very low, less than low

T - Trace amount present

ST - Slight trace, barely detected

ND - Not detected

These symbols are valid in comparisons involving a single element only. The sensitivities of various elements vary widely and therefore a quantity designated as "trace" for one might really be less than that indicated by "slight trace" for another.

Table V. lists results of the qualitative rock analyses. Only those minor elements were checked which appear in this table. None of the rare earths were analyzed. For locations of the samples see Figures 2 and Appendix A.

The major elements, Si, Al, Fe, Ca, Mg, Na and K need little discussion here. Their distribution in the granites was presented in the petrochemical chapter. From a spectrographic viewpoint they are important in that they control the distribution of certain of the trace elements. All that can be said about them here is their relative abundance in the granites. In all samples Si and Al were present as major constituents; Fe, Na and K as intermediate quantities; and Ca, Ti and Mn as minor constituents. Mg showed more variation, as sometimes it was present in small amounts, sometimes as trace element only.

Table V. Qualitative analyses of the Precambrian granites of Southeastern Missouri.
(Spectrographic determinations)

Granite type	Sample number	Mg	Sr	Ba	Ti	Zr	V	Cr	Mn	Co	Ni	Cu	Ag	Zn	Sn	Pb
Frederick-town	6	L	T	T	L	T	T	-	L	T	T	T	ST	ST	ST	T
	7	T	T	T	L	T	T	-	L	T	T	T	-	ST	ST	ST
	8	L	T	T	L	T	T	-	L	T	T	T	-	ST	ST	ST
	9	L	T	T	L	T	T	-	L	T	T	T	-	ST	ST	ST
	14	L	T	T	L	T	ST	-	L	T	T	T	-	ST	-	ST
	49	L	T	T	L	T	T	-	L	T	T	T	ST	T	ST	T
Porphyry	57	L	T	T	L	T	T	-	L	ST	T	T	-	ST	ST	ST
Doerun	18	T	T	T	L	T	T	-	L	T	T	T	-	-	ST	ST
	36	L	T	T	L	T	T	-	L	ST	T	T	-	ST	T	T
	41	L	T	T	L	T	T	-	L	T	T	T	-	-	T	T
	44	L	T	T	L	T	T	-	L	T	T	T	-	ST	T	T
	45	L	T	T	L	T	T	-	L	ST	T	T	-	-	T	T
	47	T	T	T	L	T	ST	-	L	T	T	T	-	ST	ST	T
	48	T	T	T	L	T	ST	-	L	T	T	T	ST	T	ST	T
Granite-ville	1	T	T	T	L	T	ST	-	L	T	T	T	T	-	T	T
	52	T	T	T	L	T	ST	-	L	T	T	T	-	-	ST	T
	53	T	T	T	L	T	ST	-	L	T	T	T	-	-	ST	T
	54	T	T	T	L	T	ST	-	L	T	T	T	-	-	ST	T
Ste. Genevieve	59	VL	T	T	L	T	T	-	L	ST	T	T	-	-	ST	ST
	71	L	T	T	L	T	T	-	L	ST	T	T	-	-	-	ST

Not detected in any samples: Bi, Cd, Sb, As, Au, W, Ta, Ge, Be, Cs, Li, P and B.

Legend

Symbol	Relative quantity present	Symbol	Relative quantity present
L	Low, minor constituent	ST	Slight trace
VL	Very low, less than low	-	Not detected
T	Trace		

Table V. Qualitative analyses of the Precambrian granites of Southeastern Missouri (cont'd). (Spectrographic determinations)

Granite type	Sample number	Mg	Sr	Ba	Ti	Zr	V	Cr	Mn	Co	Ni	Cu	Ag	Zn	Sn	Pb
Doerun-like	65	T	T	T	L	T	ST	ST	L	T	T	T	-	-	ST	ST
	67	T	T	T	L	T	ST	-	L	ST	T	T	-	-	ST	ST
	68	T	T	T	L	T	ST	-	L	-	T	T	-	ST	ST	ST
	60	T	T	T	L	T	ST	-	L	-	T	T	-	-	ST	ST
	62	T	T	T	L	T	ST	-	L	ST	T	T	ST	-	ST	ST
	70	T	T	T	L	T	ST	-	L	-	T	T	-	ST	ST	T
Viburnum, Pea Ridge	58	T	T	T	L	T	T	-	L	-	T	T	-	-	ST	ST
	63	L	T	T	L	T	T	-	L	T	T	T	-	-	ST	ST
	66	T	T	T	L	T	ST	ST	L	ST	T	T	-	-	ST	ST
	69	T	T	T	L	T	ST	-	L	ST	T	T	-	-	ST	ST
Knoblick	64	VL	T	T	L	T	T	ST	L	ST	T	T	ST	ST	ST	ST
Klondike	29	L	T	T	L	T	ST	-	L	ST	T	T	-	ST	ST	T
	30	L	T	T	L	T	ST	-	L	ST	T	T	-	ST	ST	T
	31	L	T	T	L	T	ST	-	L	T	T	T	-	ST	ST	T
	37	L	T	T	L	T	T	-	L	ST	T	T	-	ST	T	T
	38	L	T	T	L	T	T	-	L	T	T	T	-	ST	T	T
	39	L	T	T	L	T	T	-	L	T	T	T	-	-	T	T
	40	L	T	T	L	T	T	-	L	T	T	T	-	ST	T	T
Silvermine	15	L	T	T	L	T	T	-	L	T	T	T	-	ST	-	ST
	21	L	T	T	L	T	T	-	L	T	T	T	-	ST	ST	T
	22	L	T	T	L	T	T	-	L	T	T	T	-	ST	ST	T
	23	L	T	T	L	T	T	-	L	T	T	T	-	ST	ST	ST
	24	L	T	T	L	T	T	-	L	T	T	T	-	-	ST	ST
	26	L	T	T	L	T	T	-	L	T	T	T	-	ST	ST	ST

Not detected in any samples: Bi, Cd, Sb, As, Au, W, Ta, Ge, Be, Cs, Li, P and B.

Symbols as on previous page.

The sensitivities of the trace elements

Before discussing the results of the qualitative spectrographic analysis, it seems worth while to mention the sensitivities of the various elements.

Ahrens (1950a, p. 54) distinguishes the absolute and relative sensitivities of elements. According to his definition the absolute sensitivity is the "smallest detectable weight of element, expressed either in milligrams or in micrograms". The relative sensitivity better serves for practical purposes. It is expressed as the limit of detection of each element, it is the "lowest detectable concentration, expressed either as percentage or as parts per million".

The relative sensitivities of those elements which were analyzed and checked are tabulated in Table VI. This gives an idea as to the minimum concentration of those elements detected in the granites. On the other hand it also indicates that the absence of certain elements, such as tungsten for example, does not necessarily mean that they are not present. They may be present, but in such low concentrations as to be below the limit of their detectability.

In the following a discussion of the trace elements of the granites will be given. These are discussed under the siderophile, chalcophile and lithophile elements, as described by Goldschmidt (1937).

Table VI. Sensitivities of the Trace Elements.*

Element	Limit of detection (%)
Co	0.0002
Ni	0.0002
Sn	0.001
Cu	0.0001
Ag	0.0001-0.00003
Zn	0.01
Pb	0.001
V	0.001-0.0005
Zr	0.001
Ba, Sr	0.001-0.0001
Cr**	0.0001
Bi	0.001
Cd	0.001
Sb	0.001
As	0.01
Au	0.001
W	0.0001-0.0002
Ta	0.1-0.3
Ge	0.001-0.0001
Be	0.001-0.0001
Cs	0.01
Li	0.0001
P	0.01
B	0.001

*After Ahrens, Spectrochemical analysis, 1950.

**The elements below Cr were not detected in the analyzed specimens.

Siderophile elements

The siderophile elements are characterized by an affinity for metallic iron. They are preferably enriched in the nickel-iron core (siderosphere). Their affinity for oxygen and sulphur is relatively weak.

Nickel. (Ni^{o} -r1.24 -c12) and

(Ni^{2+} - r0.69 - c6 - e220 - S: Mg^{2+} r0.66, Fe^{2+} r0.74).*

Nickel is pronouncedly a siderophile element, but in the ionized state and in the presence of sulphur and arsenic, it shows a chalcophile tendency. Nickel reaches its greatest enrichment in magmatic sulphides. But the normal igneous rocks of the main stage of magmatic crystallization are regularly cobalt and nickel bearing also. Nickel is more strongly enriched in ultrabasic rocks, while in granites its value is given as only 2.4 g/ton (Rankama & Sahama, 1950, p. 682).

Part of the nickel content of igneous rocks originates from small quantities of common sulphide minerals, such as pentlandite, pyrrhotite and pyrite. However, the bulk of nickel is incorporated in silicate

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*A standard geochemical description will follow each element. Data of above are after Green (1959). First the element and its ionic charge is given (Ni^{2+}), followed by the ionic radius expressed in Angstrom units (r0.69), co-ordination (c6), electronegativity expressed in kilocalories/gram-atom (e220), finally substitution possibilities are listed with the ionic radius of the substituted element (S: Mg^{2+} r0.66, Fe^{2+} r0.74).

minerals and is concealed in their structures. This shows the oxyphile character of nickel in the upper lithosphere. (The terms oxyphile and sulphophile were introduced by Rankama and Sahama (1950, pp. 95-96) in their geochemical classification. It is based on the quantitatively most important manner of occurrence of the elements in the lithosphere. Oxyphile refers to elements occurring predominantly combined with oxygen in oxides, silicates, carbonates, etc. The crystal structure of these minerals is characterized by ionic bonds. The sulphophile elements occur preferentially in minerals free of oxygen, mostly in sulphides, selenides, tellurides, native elements, etc. Covalent or metallic bonds prevail in the crystal structures of these minerals).

In the silicate mineral structures nickel may substitute for Mg^{2+} and Fe^{2+} and may become enriched in the early crystallized magnesian and ferromagnesian minerals. Olivine and hypersthene are the main nickel-bearing minerals of igneous rocks. Lower nickel content occurs in augite, amphibole and biotite. Olivine may contain up to 0.5% nickel, amphibole and biotite only 0.2%.

In granites nickel is almost quantitatively contained in biotite. The feldspars are devoid of this metal.

Each of the analyzed granites contained nickel in trace amounts. Yet, according to Ahrens (1950a, p. 218) in granite-like rocks nickel is present in such low concentrations that it is below the limit of its detection, 0.0002%. The persistence of nickel in the granites of Southeastern Missouri is a peculiar feature.

Cobalt. (Co^{o} - r1.26 - c12); (Co^{2+} -r0.72 - c6 - e200 - S: Fe^{2+} r0.74, Mg^{2+} r0.66, and (Co^{3+} - r0.63 - c6 - e260). Cobalt is similar to nickel in behavior. It is first of all siderophile, characterized by metallic bonds. But as a bivalent cation it exhibits sulpho-arsenophile character with semi-metallic bonds, and when trivalent, its oxyphile property is predominant with ionic bonds.

Cobalt is a much less abundant element than nickel and occurs usually in small concentrations. The major part of cobalt in a magma is removed in the early stages of crystallization and therefore basic and ultrabasic rocks are more enriched in it than the silicic rocks. The Co : Ni ratio, however, is the greatest in the granites. The concentration of cobalt in granites is given as 8 g/ton (Rankama & Sahama, 1950, p. 682).

Besides being present in small concentrations in the common sulphide minerals, cobalt replaces diadochically Fe^{2+} and Mg^{2+} in mineral structures. Cobalt is more likely to substitute for ferrous iron, since its ionic radius is closer to that than to that of magnesium. According to Mason (1952) the Co : Fe ratio is greatest in the early formed minerals and gradually decreases with increasing fractionation. The Co : Mg ratio on the other hand was found to be practically constant throughout a rock series. It is because the effective radius of cobalt is somewhat less than the one given above, and apparently is almost identical with that of magnesium. The early formed magnesian and ferromagnesian minerals, especially olivine, are therefore the main seats of cobalt in igneous rocks.

Twenty-eight samples of the analyzed rocks had cobalt in trace amounts. All of the samples of the Fredericktown, Silvermine and Graniteville types showed this relationship.

The Doerun type granites exhibited a wider range of variation in their cobalt content. No cobalt was detected in sample No. 58 of Ste. Genevieve County, No. 60 from the Higdon area, No. 68 from St. Joe's new Mine LaMotte shaft and No. 70 from the Coldwater quadrangle. All these samples are located in the eastern and southern marginal phases of the igneous area.

Slight traces of cobalt were detected in the following Doerun type granites: Nos. 59 and 71 from Ste. Genevieve County, No. 62 from the Higdon area, Nos. 36, 45, 64 and 67 from St. Francois County, and finally Nos. 66 and 69 from the far western part of the area. The rest of the Doerun samples had cobalt in trace.

Samples of the Klondike granite also displayed a variance in cobalt content. Samples Nos. 29, 30 and 37 contained it in slight trace, the rest of them in trace.

The relatively lesser amount of cobalt in the Doerun and Klondike granites is probably due to the lower amount of mafic minerals in them. These would be the main carriers of this element.

<u>Tin.</u> (Sn^{o} - r1.59 - c12); (Sn^{2+} - r0.93 - c6) and (Sn^{4+} - r0.71 - c6 - e235).

Tin behaves rather irregularly in nature. The ionic radius of Sn^{4+} is so small that despite the nature of its outer electron shell it is less polarizable and forms stable compounds with oxygen (SnO_2, cassiterite). The Sn^{4+} is therefore oxyphile. The Sn^{2+}, however, according to its larger ionic radius is sulphophile and crystallizes hydrothermally with the chalcophile elements. Despite this fact, tin is usually classified as a siderophile element.

Among the igneous rocks tin is most typically found in granites. Its value varies between 56 and 80 g/ton. Tin is more characteristically associated with the very acidic alkali granites. In these it may reach a concentration of 0.01%.

In silicate rocks tin is found in cassiterite and may also replace a number of elements in silicate structures. It tends to concentrate in micas. Tourmaline, plagioclase and fluorite of pneumatolytic origin may also carry tin.

Nine granite samples from Southeastern Missouri contained tin in trace amounts. One of these was from Sheahan quarry, near Graniteville. The rest of the samples of the Graniteville granite, however, contained tin only in slight traces. Since pegmatitic mineralization of the granite is well known at Sheahan quarry, the greater amount of tin at this locality seems readily explained.

Four samples of Doerun granite from the main outcrop area of this rock type south of Doe Run also contained tin in trace (Nos. 36, 41, 44 and 45). Four samples of Klondike granite east of this area exhibited a similar phenomenon (Nos. 37, 38, 29 and 40).

In two samples tin could not be detected: No. 14, a Fredericktown granite and No. 15, a Silvermine granite. The rest of the granite samples contained tin in slight traces.

Chalcophile elements

The chalcophile elements are characterized by an affinity for sulphur. They are enriched in the sulphide-oxide shell (chalcosphere).

Copper. (Cu^{o} - r1.28 - c12); (Cu^{1+} - r0.96 - c6 - e177) and (Cu^{2+} - r0.72 - c6 - e235 - S: Mg^{2+} r0.66, Fe^{2+} r0.74). Geochemically copper has a mainly chalcophile character, with a slight siderophile tendency. It is the most abundant chalcophile element in the earth's crust. Its distribution in igneous rocks is very characteristic and conforms well with its chalcophile property. The average copper content (Szadeczky, 1955, p. 261) for different types of igneous rocks is:

Basic igneous rocks................	150 g/ton
Intermediary igneous rocks	40 g/ton
Acidic igneous rocks	15 g/ton

According to these data not much copper is expected to occur in the granites. However, copper is present in traces in all the analyzed samples. The actual amount of the element is not known since quantitative determinations have not been made. According to Ahrens (1950b, p. 143) in an average granite the copper content would be around 0.005%. The consistency of copper on the other hand does not necessarily mean that the element is present in considerable amounts. Its spectrochemical sensitivity is very high (detection limit 0.0001% and sometimes less) and because copper is such a widespread element its detection in the granites is not so surprising.

Chalcopyrite is the mineral which is abundant enough to be responsible for most of the copper present in the rocks, but it may also be possible that in some instances copper enters the structures of rock forming silicates, replacing Mg^{2+} and Fe^{2+}. Alkali feldspars may also conceal it. Consequently copper seems to be sulphophile but its character is not very pronounced.

Silver. (Ag^{o} - rl. 44 - cl2); (Ag^{1+} - rl. 31 - c8 - e175) and (Ag^{2+} - r0. 89 - c6).

Silver, like copper, is a chalcophile element with a much weaker tendency to siderophile than the other metal. Silver is much less abundant in the earth's crust than copper. According to its chalcophile character silver avoids the pre- and main phases of crystallization.

The distribution of silver in igneous rocks is variable but never more than 10 g/ton. The value in granites is between 0.9 and 7.7 g/ton (Rankama & Sahama, 1950, p. 705).

In the analyses of the granites of Southeastern Missouri silver proved to be rather scarce. In the Klondike and Silvermine granites it was not detected at all. The metal has a high spectrochemical sensitivity (limit of detection : 0.0001-0.00003%), but because of its extremely low content in common silicate rocks, it can usually not be detected. Also, according to Ahrens (1950a) in the presence of much Fe, Co and Ni the most sensitive lines of silver are unusually weak. The mentioned elements are relatively abundant in the granites.

Sample No. 1 from Sheahan quarry contains the greatest amount of silver, here indicated as trace. The rest of the Graniteville granites did not contain any measurable quantity of this metal. The presence of silver in the quarry may be explained by the known mineralization in the area.

Two samples from the northern part of Stono Mountain in St. Francois County (Nos. 48 and 49) contained silver in slight traces. One of these is a Fredericktown granite, the other is Doerun. These samples are located in the northwestern part of the area.

In the eastern part of the sampled area three samples contained silver in slight traces: No. 6, a Fredericktown granite, No. 64, from Knoblick Mountain, and No. 62, a Doerun type granite from the Higdon area.

Silver is mostly contained in sulphides. It is not known to occur in the structures of rock making silicates. Its sulphophile character is therefore stronger than that of copper.

<u>Zinc.</u> (Zn^{o} - r1.36 - c12 - e208); (Zn^{2+} - r0.74 - c6 - S: Fe^{2+} r0.74, Mn^{2+} r0.80, Mg^{2+} r0.66).

Zinc is predominantly chalcophile. In the upper lithosphere it is classified among the oxyphile elements.

A few years ago zinc was considered much more abundant than it actually is. Rankama and Sahama (1950) estimated its average content in igneous rocks as 132 g/ton. According to later studies of Vinogradov and Wedepohl (Szadeczky, 1955, p. 266) it was found to be only 50 g/ton. Zinc is generally more abundant in intermediary and basic igneous rocks, while in granites its value is only 34 g/ton.

Among the common rock making minerals biotite shows the highest content of zinc, but hornblende and pyroxene can also carry it. In these minerals zinc usually takes the place of Fe^{2+}, Mn^{2+} and Mg^{2+} in the structure, since its ionic radius approximates the radii of those ions. Furthermore, thermochemical studies indicate that zinc cannot normally be incorporated in feldspars. Sphalerite, the most common and most important of the sulphide minerals of zinc, is rather rare among the accessory sulphides of ordinary igneous rocks, and it is not known to what extent zinc is able to enter the structures of pyrite and chalcopyrite under conditions of formation of these minerals in nature.

Traces of zinc were found in samples Nos. 48 and 49 from north of Stono Mountain. These are the same samples which contain slight traces of silver. But sample No. 1 from Sheahan quarry, which seemed to contain the most silver of all the samples did not contain any zinc. In this respect all samples of the Graniteville granite behaved similarly.

The following Doerun granites contained slight traces of zinc: Nos. 36, 44 and 47 from the main outcrop area. The rest of these granites did not have zinc. Slight traces of this element were found in most of the Klondike and Silvermine granites with the exception of sample Nos. 39 and 24, respectively, which lacked in zinc. All the Fredericktown granites and the granite porphyry displayed slight traces of zinc. Most of the samples from the eastern margin of the igneous area, that is from Ste. Genevieve County and from the Higdon area, lacked in zinc content. The same applies to the samples from Viburnum and the Pea Ridge shaft. These include Nos. 58, 63, 66 and 69. The Coldwater granite from the south had slight traces of zinc.

Lead. (Pb^{0} - r1.74 - c12 - e245), (Pb^{2+} - r1.24 - c8 - e170), (Pb^{4+} - r0.84 - c6).

According to the Niggli-Sonder rule lead is one of the more abundant elements. It is considered to be chalcophile, though with a strong siderophile tendency. In the upper lithosphere lead shows a pronounced affinity for oxygen and hence classified as oxyphile.

In the magmatic silicate phases it mostly occurs with calcium in apatite and diopside and with potash in feldspars. According to its occurrence in potash feldspars, lead is more strongly enriched in acidic igneous rocks (9-30 g/ton) than in basic ones (5 g/ton), (Szadeczky, 1955, p. 284). A considerable amount of lead in igneous rocks occurs as galena.

Lead is present in each of the granite samples in trace or slight trace amounts. Traces of lead were detected in the Graniteville, Klondike and Doerun granites from the main outcrop area. The Coldwater granite also contained more lead. In the Fredericktown and Silvermine granites lead was relatively less, with the exception of samples Nos. 6, 49, 21, and 22, respectively. The samples from Ste. Genevieve County, the Higdon area and from the western part (Viburnum, Pea Ridge) contained it in slight traces.

Of interest is a comparison of the lead and silver content of the granites and that of the ore deposits of the Lead Belt here. It is known that in ore deposits related to intrusive rocks most of the silver content crystallizes in galena. Lead and silver therefore are generally closely associated with each other. It has been observed that lead was present in considerable traces in all of the analyzed samples. Silver on the other hand was relatively rare, or absent. The same thing applies to the ore deposits of Southeastern Missouri. Very little or no silver is associated with the rich lead deposits. In this respect the granites behave similarly to the lead ore deposits found near them in post-granite sediments.

Lithophile elements

The lithophile elements are characterized by a strong affinity for oxygen. They are enriched in the silicate crust (lithosphere).

<u>Vanadium.</u> (V^{3+} - r0.74 - c6 - e235 - S: Fe^{3+} r0.64),

(V^{4+} - r0.63 - c6 - e280 - S: Fe^{3+} r0.64, Al^{3+} r0.51, Ti^{4+} r0.68),

(V^{5+} - r0.56 - c4 - e315 - S: Fe^{3+} r0.64, Al^{3+} r0.51, P^{5+} r0.33).

The general geochemical character of vanadium is pronouncedly lithophile with a relatively distinct siderophile tendency. It is one of the more abundant trace elements.

Goldschmidt gives its concentration in average igneous rocks as 130 g/ton (Rankama & Sahama, 1950, p. 594). The highest vanadium content is found in those igneous rocks which formed during the initial steps of the main stage of crystallization. Leutwein gave its value in granites and granodiorites as varying between 1 and 20 g/ton (Rankama & Sahama, 1950, p. 596). It can be detected in rocks down to about 0.001-0.0005%.

Vanadium occurs in three stable oxidation states in igneous surroundings, namely as tri-, quadri-, and quinquevalent V. Because of this reason many possibilities of diadochic substitution of various elements by vanadium in mineral structures exist.

The vanadium content of igneous rocks is largely found in magnetite and ilmenite, where it replaces Fe^{3+} and Ti^{4+}. It also occurs in titaniferous magnetite, sphene, rutile and in apatite, in the latter V^{5+} replacing P^{5+}.

The dark constituents, like pyroxenes, amphiboles and micas, may all contain small amounts of vanadium, here V^{4+} and V^{5+} ions replacing Fe^{3+} and Al^{3+}. The diadochic replacement of Fe^{3+} by the V^{3+} ion is not very probable, as the latter is a strong reducing agent and would reduce ferric iron to the ferrous state. The feldspars show a lack of vanadium content. Partly this is the reason why there is more vanadium in basic rocks than in acidic ones.

All the samples of the Graniteville granites contained only slight traces of vanadium. The Doerun and Klondike types showed a variation in their vanadium content. Nos. 29, 30 and 31 of the Klondike granite had a slight trace of this element, while Nos. 37, 38, 39, and 40 contained it in traces. The distribution of tin was similar to the vanadium in the Klondike granites. The first three samples are located on the southern part of the Klondike granite outcrop area, the other four are from the north.

Samples Nos. 36, 41, 44, and 45 from the main outcrop area of the Doerun granite contain vanadium in traces, samples Nos. 47 and 48 in slight traces. Sample No. 18 contained it in trace, as well as sample Nos. 59 and 71 from Ste. Genevieve County, No. 58 from Viburnum, and No. 63 from the Pea Ridge shaft.

All the Fredericktown granites except sample No. 14 contained vanadium in trace. All Silvermine granite samples had it in trace, as well as the porphyry.

Sample Nos. 60 and 62 from the Higdon area contained vanadium in slight traces only. Sample Nos. 65, 66, 67, 68, 69, and 70 behaved similarly.

Zirconium. (Zr^{o} - rl. 60 - cl2 - e200), (Zr^{4+} - r0. 79 - c6). Zirconium is strongly lithophile, in the upper lithosphere it is oxyphile. It is a rather common trace element of igneous rocks, but shows a tendency to become more enriched in the last rocks to crystallize during the main stage of crystallization, namely in granites. Here its value may be as high as 460 g/ton (Rankama & Sahama, 1955, p. 566).

The main carrier of zirconium in igneous rocks is the mineral zircon. In some granites and their pegmatites another zirconium mineral, baddeleyite (ZrO_2) may be the source of zirconium content, but this mineral is relatively rare. Generally very little zirconium is incorporated in the femic constituents of igneous rocks.

All the analyzed samples contained traces of zirconium.

Barium and Strontium. (Ba^{2+} - rl. 43 - cl0 - S: K^{1+} rl. 42), (Sr^{2+} - rl. 16 - c8 - S: Ca^{2+} rl. 03).

The alkaline-earth metals barium and strontium are strongly lithophile, in the upper lithosphere they are oxyphile. Both are among the most abundant trace elements of igneous rocks.

The highest content of barium and strontium is found in such alkalic rocks as syenites and nepheline-syenites. The basic igneous rocks are poorest in these metals. The amounts of strontium and barium in the Rapakivi granites of eastern Fennoscandia is given by Sahama (1950) as 100 and 900 g/ton, respectively.

Both strontium and barium only exceptionally form independent minerals in igneous rocks. They are mainly concealed in the rock making silicates. Although the two metals chemically resemble each other, their manner of occurrence shows considerable difference. Strontium usually replaces calcium and sometimes potassium in the mineral structure. Barium on the other hand usually substitutes for potassium. Therefore strontium is present both in the plagioclases and in the potash-feldspars, but significant amounts of barium are found only in the potash-feldspars. Barium may replace potassium diadochically in the mica structure, but because of the low calcium content strontium is less readily associated with these minerals. Strontium may substitute for calcium in the apatite structure also.

All the analyzed samples showed traces of both metals.

Both barium and strontium are relatively easily detected, since they have a high spectral sensitivity. The limit of detection is about 0.001-0.0001%.

Chromium. (Cr^{o} - r1.28 - c12), (Cr^{3+} - r0.63 - c6 - e250 - S: Fe^{3+} r0.64, Al^{3+} r0.51).

Chromium is considered to be a lithophile element, but it may also behave as a siderophile one when O-valent, and as chalcophile when O-3-valent. It is a rather scarce element in the upper lithosphere.

The concentration of chromium in different types of igneous rocks varies greatly. According to Szadeczky (1955, p. 374) it is:

Ultrabasic rocks.................	3400 g/ton
Gabbro (diabase)	340-410 (220) g/ton
Granite	2-7 g/ton

In granite rocks the concentration may be so low that despite the very high sensitivity of the element (detection limit 0.0001%), it may not be detectable.

In the ultrabasic rocks chromite is the main carrier of chromium. In fact, this is the first mineral to separate during the normal crystallization of calc-alkalic magmas. The chromium members of the spinel group will also carry it. None of these minerals, however, is a normal constituent of acidic rocks.

Geochemically more significant is the chromium which is present only in traces in the structures of rock forming silicates. It may replace ferric iron and aluminum diadochically, and less commonly also ferrous iron and magnesium. Consequently, chromium more readily enters into the structures of ferromagnesian minerals, especially olivines (Forsterite rich), augites and hornblendes, but Bray (1942) reports a high trace amount of this metal in the biotites and muscovites of the granites he studied.

All but three of the analyzed granite samples from Southeastern Missouri were deficient in chromium. Those which contained it in slight trace were Nos. 64, 65, and 66 from differing localities in the area.

Elements not detected

The following elements could not be detected in the granite samples: Bi, Cd, Sb, As, Au, W, Ta, Ge, Be, Cs, Li, P, and B. Most of these elements are very difficult to detect in common silicate rocks. The reason for this is partly due to their very low concentration in such rocks and also their poor sensitivity. The latter includes such elements as Bi, Cd, Sb, As, Au, and Ta. By concentration of the samples, such as dissolving the silica by HF acid, they could possibly be detected. This procedure, however, was not used in this study.

Tungsten is usually not detectable in rocks because its concentration is below the limit of detection. Phosphorus and boron were also not detected in the granites. The most sensitive lines of these elements were masked by iron lines, therefore they could not be positively established. The surest and most sensitive spectral lines of lithium are located outside the range used in this work, at 6707.8 and 6103.6 A. Consequently, in order to ascertain it's presence in the granites, separate analyses should be run in a higher wave length range.

Comparison of the Trace Element Content of the Granites of Southeastern Missouri with Granites of Other Areas

According to Ahrens (1950b, p. 143) the following minor elements can usually be detected spectrochemically in granites: Be, Zr, La, Y, Nd, Ba, Sr, Rb, Cs, Li, Ga, Pb, Ni, Co, Cr, V, Sc, Cu, Ge, Tl, Cb, Ag, Sn, B, and F. Of these twenty-five elements, eleven were found in the Precambrian granites of Southeastern Missouri. Be, Cs, Li, Ge, and B were not detected in any of the samples. The rest of the elements were not determined. Only zinc, which Ahrens does not mention as a typical constituent of granitic rocks, was found in some samples.

Reference has already been given to the investigations of Bray (1942) and Shimer (1943) on the granites of Colorado and New England, respectively. The trace element content of the Missouri granitic rocks is generally not much different from these districts. A striking difference, however, is the consistency of copper in the Missouri rocks. As already mentioned, copper occurred in all the samples, while the Colorado granites contained no trace of it. In the New England granites only a few samples contained copper. Since careful precautions were taken during the preparation of the samples and the analytical procedure, it is highly improbable that the copper content is due to contamination.

Shimer does not mention Co, Ni, Sn, Ag, Zn, and Pb in the New England granite analyses. A separate analysis of the granite micas revealed the presence of Co, Ni, and Zn, but only in the biotites. The muscovites were devoid of these elements. He did not report Sn, Ag, and Pb from these rocks, but did note that Ga, La, Sc, and Y were present. The areal variation in the Ba, Sr, and Mg content was insignificant. Zirconium showed slight variations according to the zircon content of the rocks. He found a close correlation between amounts of V and Cr. This is not true of the Missouri rocks. While V was quite persistent in these rocks, Cr was absent in all but three samples. Shimer also found that the higher the biotite content was in the granites, the more abundant the minor elements. This is generally true of the Missouri rocks also.

The Colorado rocks contained Co and Ni, but only those oldest in the Precambrian series. Ag and Zn were noted in very small traces in but a few samples. Lead was more abundant in the younger Precambrian rocks. Bray concludes from this that the lead content is not due to radioactive disintegration, since in this case it would be more abundant in the older rocks. Ba and Sr were noted in spectrochemically large quantities, but as all the rocks were acid, no striking differences in the Ba and Sr content were observed. Zirconium was found in variable amounts, as a function of the amount of zircon present. The distribution of V and Cr was similar, as in the case of the New England granites. They both substitute for ferric iron, therefore were found in largest amounts in those samples where ferric iron was abundant. The Colorado rocks also contained Sc, Y, La, Ce, and Nd.

Summarizing the differences, the Missouri rocks differ from the two other areas in their abundance in copper; in the relatively frequent occurrence of tin; in the rareness of chromium and the lack of correlation between chromium and vanadium; in the much higher abundance of zinc; and in abundance in lead accompanied with very little silver. Table VII illustrates the comparison of the trace element content between the three different areas.

Summary on Spectrographic Analysis

Most of the minor elements occur in each rock type. To set up a scheme on the basis of the presence or absence of such elements alone is therefore not convenient. A scheme based on the relative amounts of

Table VII. Comparison of Trace Elements of Granites from Colorado (Bray), New England (Shimer), and Southeastern Missouri (this Report).

Trace Element	Colorado Granites			SE Missouri Granites			New England Granites	
	A	ST	T	A	ST	T	A	T
Mg			—			—		—
Sr			—			—		—
Ba			—			—		—
Ti			—			—		—
Zr			—			—		—
V		—	—		—	—		—
Cr		—	—	—	—			—
Mn			—			—		—
Co	—	—			—	—	—	
Ni	—	—				—	—	
Cu	—					—	—	
Ag	—	—		—	—		—	
Zn	—			—	—		—	
Sn	—				—		—	
Pb	—	—			—	—	—	
Be	—			—			ND	
Cs	ND			—			ND	
Li	ND			—			ND	
Ge	—			—			ND	
B	ND			—			ND	
Ga	ND			ND				—
La	—	—		ND				—
Sc	—	—		ND				—
Y	—	—		ND				—
Ce	—	—		ND			—	
Nd	—	—		ND			—	

Symbols:

- A absent
- ST slight trace
- T trace
- ND not determined

minor elements present, combined with the one just mentioned, will more clearly bring out the characteristics of the different rock types.

The elements which show variation from rock type to rock type and therefore are useful in such consideration are the following: Mg, V, Co, Zn, Sn, and Pb.

Although magnesium was noted in the graphite electrodes, its relative quantity in the granites probably exceeded that of the amount of impurity. The selection of magnesium as an index trace element therefore is quite justified.

The Fredericktown granite and the porphyry are characterized by a larger amount of Mg (L), more V and Co (T), and relatively less Zn, Sn, and Pb (ST). In respect to these six elements the Silvermine granite behaves almost identically. Though silver was detected in slight traces in some of the Fredericktown granites, the Silvermine granite was completely devoid of it.

Mg is not a good index element for the Doerun granite; its amount varies between "Trace" and "Low". V and Co in the Doerun granite, as in the Fredericktown and Silvermine, is contained mostly in traces. Zn cannot always be detected and Sn seems to be present in higher quantities (T). The Doerun granite has high amounts of Pb (T).

The Graniteville granite, which actually belongs to the Doerun mineralogical type, contains Mg in trace, V in slight trace, Co in trace, is devoid of Zn, has less Sn, and is abundant in Pb (T).

The different granites, indicated as "Doerun-like", which are also closely related petrologically to the typical Doerun granites of the main outcrop area, contain traces of Mg, slight traces of V and Sn, and differ from the Graniteville granite in their much lower amount or even absence of Co, the occurrence of Zn in a few of the samples, and in their much smaller amount of Pb (ST).

For the granites from Viburnum and Pea Ridge (also Doerun type) Mg, V, and Co are not good index elements. They do not contain Zn, and their Sn and Pb content is small (ST).

The Klondike granite has Mg (L), V, Co, and Sn in varying amounts (T-ST), less Zn (ST), and much Pb (T).

The following Table VIII shows the distribution of the index elements in the granite types.

Table VIII. Index Trace Elements in the Southeastern Missouri Granite Types

Rock	Mg	V	Co	(Ag)	Zn	Sn	Pb
Fredericktown	L	T(ST)*	T	O-ST	ST(T)	ST(O)	ST(T)
Doerun	L-T	T(ST)	T(ST)	O(ST)	ST-O	T-ST	T
Graniteville	T	ST	T	O(T)	O	ST(T)	T
Doerun-like	T	ST	O-ST	O(ST)	O-ST	ST	ST
Viburnum, Pea R.	T(L)	ST-T	ST(T,O)	O	O	ST	ST
Klondike	L	T-ST	T-ST	O	ST	T-ST	T
Silvermine	L	T	T	O	ST(O)	ST(O)	ST(T)

*Letters in parentheses mean that only one sample contained the element in the indicated amount.

SUMMARY AND CONCLUSIONS

Forty-four petrographic, 27 petrochemical, and 44 spectrographic analyses of Precambrian granitic rocks from Southeastern Missouri warrant the following conclusions:

1. The granites exhibit a close genetic relationship as demonstrated by petrochemical studies using the Niggli method. The original granite magma was acidic, salic, relatively alkali rich and lime poor. The Doerun, Graniteville and Klondike granites are in the aplitgranitic, the Fredericktown granites and granite porphyries in the aplitgranitic and engadinitgranitic, the Knoblick granite in the granodioritic, and the Silvermine granite in the yosemititgranitic magma type. All the rocks belong to the calc-alkalic petrographic province.

2. Based on the Johannsen classification, the rocks can be classified petrographically as leucogranites, granites, alaskites, kalialaskites, sodaclasegranites and adamellites. They are the product of essentially two phases of magmatic intrusion and magmatic differentiation.

3. Qualitative spectrographic analyses revealed the presence of the following minor elements: Mg, Sr, Ba, Ti, Zr, V, Cr, Mn, Co,

Ni, Cu, Ag, Zn, Sn, and Pb. Based on the presence or absence of these, and the relative amounts of minor elements present, a scheme was set up to bring out the characteristics of the different rock types. Mg, V, Co, Zn, Sn, and Pb were selected as index trace elements.

The Fredericktown granite, the granite porphyries, the Knoblick granite and the Silvermine granite are characterized by a larger amount of Mg, V, and Co. They contain less, or lack in Zn, Sn, and Pb. The Doerun, Graniteville and Klondike granites are also relatively high in V and Co. Zinc is not always present in these latter ones, but they have more Sn and Pb than the other granite types. The greater abundance of tin and lead in the Doerun granites correlates well with world examples of these elements associated with the more acidic rocks within a magma province.

Compared with granites from Colorado and New England, the Missouri granites are characterized by a consistency of copper, a relatively frequent occurrence of tin, lead and zinc, and a rareness of Cr and Ag.

APPENDIX A

Key to the Location of the Collected Samples

No.	Field No.	Location				Rock Type
1	1153-3-1	SW 1/4 SW 1/4	sec. 11,	T34N,	R3E	Graniteville granite
2	1153-5-2	NW 1/4 SW 1/4	sec. 21,	T34N,	R6E	Fredericktown granite
3	1153-5-3	NW 1/4 SW 1/4	sec. 21,	T34N,	R6E	Fredericktown granite
4	1153-5-4	SW 1/4 SW 1/4	sec. 21,	T34N,	R6E	Fredericktown granite
5	1153-5-5	SW 1/4 SW 1/4	sec. 21,	T34N,	R6E	Fredericktown granite
6	1153-6-3	NW 1/4 NE 1/4	sec. 21,	T34N,	R6E	Fredericktown granite
7	1153-6-5	SW 1/4 SE 1/4	sec. 28,	T34N,	R6E	Fredericktown granite
8	1153-7-1	NE 1/4 SW 1/4	sec. 26,	T34N,	R6E	Fredericktown granite
9	1153-7-2	N 1/2 NE 1/4	sec. 2,	T33N,	R6E	Fredericktown granite
10	1153-7-3	NW 1/4 SW 1/4	sec. 35,	T34N,	R6E	Fredericktown granite
11	1153-7-4	NE 1/4 SW 1/4	sec. 28,	T34N,	R6E	Fredericktown granite
12	1153-8-1	NW 1/4 SE 1/4	sec. 29,	T34N,	R7E	Fredericktown granite
13	1153-8-2a	SE 1/4 S 1/2	sec. 6,	T33N,	R7E	Fredericktown granite
14	1153-8-2b	SE 1/4 S 1/2	sec. 6,	T33N,	R7E	Fredericktown granite
15	1153-9-1	NE 1/4 SE 1/4	sec. 9,	T33N,	R6E	Silvermine granite
16	1153-9-2	NE 1/4 SE 1/4	sec. 9,	T33N,	R6E	Silvermine granite
17	1153-9-3a	SE 1/4 S 1/2	sec. 4,	T33N,	R6E	Doerun granite
18	1153-9-3b	SE 1/4 S 1/2	sec. 4,	T33N,	R6E	Doerun granite
19	1153-9-4	NE 1/4 N1/2	sec. 4,	T33N,	R6E	Doerun granite
20	1153-10-1	NE 1/4 N 1/2	sec. 4,	T33N,	R6E	Doerun granite
21	1153-10-2	SE 1/4 NW 1/4	sec. 7,	T33N,	R6E	Silvermine granite
22	1153-10-3	SE 1/4 SE 1/4	sec. 12,	T33N,	R5E	Silvermine granite
23	1153-11-1	SE 1/4 SW 1/4	sec. 31,	T34N,	R5E	Silvermine granite
24	1153-11-2	SE 1/4 SW 1/4	sec. 32,	T34N,	R5E	Klondike granite
25	1153-11-3	SE 1/4 SW 1/4	sec. 32,	T34N,	R5E	Aplite dike
26	1153-11-4	N 1/2	sec. 3,	T33N,	R5E	Silvermine granite
27	1153-11-5	N 1/2	sec. 2,	T33N,	R5E	Rhyolite
28	1153-11-6	N 1/2	sec. 1,	T33N,	R5E	Doerun granite
29	1153-12-1	SW 1/4 NW 1/4	sec. 31,	T34N,	R6E	Klondike granite
30	1153-12-2	SW 1/4 NW 1/4	sec. 30,	T34N,	R6E	Klondike granite
31	1153-12-3	SW 1/4 SW 1/4	sec. 24,	T34N,	R5E	Klondike granite
32	1153-12-4	NE 1/4 SW 1/4	sec. 23,	T34N,	R5E	Klondike granite
33	1153-12-5	SW 1/4 NE 1/4	sec. 26,	T34N,	R5E	Klondike granite
34	1153-12-6	NW 1/4 N 1/2	sec. 1,	T33N,	R5E	Doerun granite
35	1153-13-1	SE 1/4 SE 1/4	sec. 20,	T34N,	R5E	Doerun granite
36	1153-13-2	SE 1/4 NW 1/4	sec. 16,	T34N,	R5E	Doerun granite

No.	Field No.	Location	Rock type
37	1153-13-3	SE 1/4 SE 1/4 sec. 9, T34N, R5E	Klondike granite
38	1153-13-4	NE 1/4 NE 1/4 sec. 10, T34N, R5E	Klondike granite
39	1153-13-5	sec. 35-36, T35N, R5E	Klondike granite
40	1153-13-6	SW 1/4 NW 1/4 sec. 8, T34N, R6E	Klondike granite
41	1153-14-1	NW 1/4 SE 1/4 sec. 24, T34N, R4E	Doerun granite
42	1153-14-2	NW 1/4 NW 1/4 sec. 14, T34N, R4E	Doerun granite
43	1153-14-3	SE 1/4 SW 1/4 sec. 6, T34N, R5E	Doerun granite
44	1153-14-3a	SE 1/4 SW 1/4 sec. 6, T34N, R5E	Doerun granite
45	1153-14-4	NW 1/4 NE 1/4 sec. 29, T35N, R5E	Doerun granite
46	1153-14-5	SW 1/4 SW 1/4 sec. 19, T35N, R5E	Doerun granite
47	1153-15-1	SE 1/4 SE 1/4 sec. 26, T35N, R4E	Doerun granite
48	1153-15-2	S 1/2 sec. 3, T35N, R4E	Doerun granite
49	1153-15-3	S 1/2 sec. 3, T35N, R4E	Stono granite
50	1153-15-4	Center of sec. 14, T35N, R3E	Buford gr. porph.
51	1153-15-5	SW 1/4 NE 1/4 sec. 13, T35N, R3E	Buford gr. porph.
52	1153-16-1	NE 1/4 SW 1/4 sec. 22, T34N, R3E	Graniteville granite
53	1153-16-2a	SE 1/4 NE 1/4 sec. 10, T34N, R3E	Graniteville granite
54	1153-16-2b	SE 1/4 NE 1/4 sec. 10, T34N, R3E	Graniteville granite
55	1153-16-3	SE 1/4 NE 1/4 sec. 10, T34N, R3E	Graniteville granite
56	1153-17-1	SW 1/4 SW 1/4 sec. 27, T33N, R3E	Carvery Creek gr. porph.
57	1153-17-2	SE 1/4 SE 1/4 sec. 28, T33N, R3E	Carvery Creek gr. porph.
58	1153-17-3	N 1/2 sec. 16, T35N, R2W	Viburnum
59	1153-18-1	NW 1/4 sec. 8, T36N, R7E	Ste. Genevieve
60	1153-18-2	SE corner of sec. 1, T33N, R7E	Higdon
61	1153-18-3	NW 1/4 NW 1/4 sec. 8, T33N, R8E	Higdon
62	1153-19-1	SW corner of sec. 4, T33N, R8E	Higdon
63	1153-S-1*	Pea Ridge Shaft	Pegmatite
64	1153-S-2	sec. 8, T34N, R6E	Knoblick granite
65	1153-S-3	sec. 7, T36N, R4E	Doerun type granite
66	1153-S-4	Bottom level of shaft #27 NW 1/4 sec. 15, T35N, R2W	Doerun type granite
67	1153-S-5	From drillhole SW 1/4 sec. 16, T36N, R5E	Doerun type granite
68	1153-S-6	From St. Joe's new Mine LaMotte shaft sec. 35, T34N, R7E	Doerun type granite
69	1153-S-7	From drillhole sec. 1, T36N, R2W	Doerun type granite
70	1153-S-8	SE 1/4 sec. 13, T30N, R5E	Coldwater granite
71	1153-S-9	Jonca Creek, Ste. Genevieve County sec. 7, T36N, R7E	Ste. Genevieve

*The samples using an S designation were contributed by Dr. F. G Snyder, Chief Geologist of the St. Joseph Lead Company.

APPENDIX B

Key to the Location of the Chemical Analyses

Sample No.	*	Location				Granite Type
27c	41	NW 1/4 SE 1/4 SW 1/4	sec. 22,	T34N,	R3E	Graniteville
28c	42	East section 1.	sec. 31,	T33N,	R6E	Doerun
30c	44	SW 1/4 SW 1/4	sec. 11,	T34N,	R3E	Graniteville
31c	45	S 1/2 NE 1/4 SW 1/4	sec. 36,	T35N,	R5E	Klondike
32c	46	SE 1/4 SW 1/4 NE 1/4	sec. 36,	T35N,	R4E	Doerun
33c	47	NW 1/4 SW 1/4 SW 1/4	sec. 11,	T34N,	R3E	Graniteville
34c	48	SE cor. NE 1/4 SW 1/4	sec. 25,	T33N,	R7E	Doerun
35c	49	N 1/2	sec. 5,	T33N,	R6E	Doerun
36c	50	NW 1/4 E 1/2 lot 3 E.	sec. 5,	T33N,	R6E	Doerun
37c	51	NW 1/4 SW 1/4	sec. 20,	T36N,	R4E	Doerun
38c	52	SW 1/4 NW 1/4 NW 1/4	sec. 2,	T34N,	R5E	Klondike
41c	55	NE 1/4 SW 1/4	sec. 5,	T35N,	R6E	Klondike
42c	56	NW 1/4 NE 1/4	sec. 24,	T30N,	R5E	Doerun
43c	57	SW 1/4 SE 1/4	sec. 7,	T36N,	R7E	Doerun
44c	58	W 1/2 lot 1, W	sec. 6,	T33N,	R7E	Fredericktown
45c	59	NE 1/4 E 1/2 lot 7 E.	sec. 2,	T33N,	R6E	Fredericktown
46c	60	W 1/2 NE 1/4	sec. 31,	T34N,	R7E	Fredericktown
48c	62	W 1/2 lot 4 E.	sec. 2,	T33N,	R6E	Fredericktown
49c	63	NE cor.	sec. 15,	T35N,	R4E	Fredericktown
51c	65	NW 1/4 NE 1/4 NE 1/4	sec. 13,	T33N,	R5E	Silvermine
53c	67	NE 1/4 NW 1/4 SW 1/4	sec. 4,	T34N,	R6E	Knoblick
54c	68	W 1/2 lot 5 E.	sec. 4,	T33N,	R5E	Doerun (?)
56c	69	W 1/2 NE 1/4 SW 1/4	sec. 14,	T35N,	R3E	Porphyry
57c	70	NE 1/4 E 1/2 lot 2 E.	sec. 4,	T33N,	R2E	Porphyry
	71	Washington County				Doerun (?)
	72	Washington County				Doerun (?)
	73	Washington County				Doerun (?)

*MGS (Missouri Geological Survey) Numbers after Hayes (1959).

APPENDIX C

Chemical Analyses of the Precambrian Granites of Southeastern Missouri

Sample No.	27c* (41)	28c (42)	30c (44)	31c (45)	32c (46)
SiO_2	77.85%	77.76%	76.81%	76.70%	76.59%
Al_2O_3	11.53	11.70	12.23	12.69	12.10
Fe_2O_3	.71	.68	.52	.46	.64
FeO	.58	.51	.41	.43	.51
MgO	.09	.10	.12	.10	.14
CaO	.73	.36	.98	.35	.53
Na_2O	3.72	3.67	3.85	3.62	3.25
K_2O	4.19	4.32	4.59	4.92	5.38
H_2O+	.26	.31	.26	.40	.37
H_2O-	.08	.06	.01	.08	.13
TiO_2	.14	.06	.08	.06	.11
P_2O_5	.03	.00	tr.	.00	.02
MnO	.00	.01	.00	.02	.02
ZrO_2	.01		.02		
F		.14	.14	.15	.26
CO_2			.07		
S			.01		
BaO			.01		
Cr_2O_3			.00		
NiO					
Less O for F or S		-.06	-.07	-.06	-.11
TOTAL	99.92%	99.62%	100.07%	99.92%	99.94%

*Numbers in parentheses correspond to those of Hayes (1959).

Sample No.	33c (47)	34c (48)	35c (49)	36c (50)	37c (51)
SiO_2	76.44%	76.09%	76.00%	75.84%	75.64%
Al_2O_3	12.48	12.57	12.47	12.57	11.42
Fe_2O_3	.44	.96	1.59	.77	1.16
FeO	.45	.49	.61	.77	.68
MgO	.05	.04	.23	.19	.97
CaO	.95	.55	.53	.64	.31
Na_2O	3.67	3.68	4.02	3.48	3.91
K_2O	4.84	4.56	3.39	4.58	5.07
H_2O+	.13	.60	.23	.61	.34
H_2O-	.05	.07	.11	.09	.16
TiO_2	.07	.17	.11	.13	.26
P_2O_5	.00	.05	.07	.01	.05
MnO	.00	.06	.00	.03	.37
ZrO_2		.08			.04
F	.41			.12	
CO_2			.33		
S	.02				
BaO	.01				
Cr_2O_3			.00		
NiO					
Less O for F or S	-.18			-.05	
TOTAL	99.83%	99.97%	99.69%	99.78%	100.38%

	38c (52)	41c (55)	42c (56)	43c (57)	44c (58)
SiO_2	75.50%	74.27%	73.53%	72.70%	72.55%
Al_2O_3	12.74	12.12	12.12	13.97	13.09
Fe_2O_3	.46	.76	1.77	.81	1.80
FeO	1.12	1.66	1.35	1.38	1.47
MgO	.19	.18	.10	.58	.39
CaO	.63	.98	.86	1.09	.80
Na_2O	3.43	3.82	3.88	3.63	4.18
K_2O	4.66	4.24	4.85	4.74	4.51
H_2O+	.68	.65	.31	.42	.51
H_2O-	.13	.17	.11	.09	.11
TiO_2	.14	.59	.69	.29	.40
P_2O_5	.04	.07	.08	.08	.06
MnO	.05	.46	.09	.04	.04
ZrO_2			.06		
F	.13			.07	
CO_2		.03			
S					
BaO					
Cr_2O_3					
NiO					none
Less O for F or S	-.05			-.03	
TOTAL	99.85%	100.00%	99.80%	99.86%	99.91%

Sample No.	45c (59)	46c (60)	48c (62)	49c (63)	51c (65)
SiO_2	72.44%	72.42%	72.28%	70.69%	69.70%
Al_2O_3	12.75	13.82	13.82	12.64	14.80
Fe_2O_3	2.00	2.31	1.81	2.13	1.26
FeO	1.92	.55	1.50	2.01	1.80
MgO	.09	.48	.21	.85	.76
CaO	1.01	.91	.89	1.30	1.75
Na_2O	3.39	7.85	4.20	4.04	4.18
K_2O	4.32	.19	4.37	4.38	3.92
H_2O+	.49	1.05	.41	.46	.76
H_2O-	.11	.09	.16	.13	.13
TiO_2	.45	.64	.21	.52	.40
P_2O_5	.15	.12	.17	.19	.14
MnO	.05	.09	.02	.13	.07
ZrO_2	.03	.03			
F				.12	.07
CO_2					
S	.03				
BaO					
Cr_2O_3					
NiO					
Less O for F or S	-.01			-.05	-.03
TOTAL	99.22%	100.55%	100.05%	99.54%	99.71%

Sample No.	53c (67)	54c (68)	56c (69)	57c (70)	(71)
SiO_2	66.55%	64.86%	72.23%	70.71%	72.7 %
Al_2O_2	15.52	15.31	13.21	14.12	13.0
Fe_2O_3	1.57	1.63	.75	1.26	4.7
FeO	2.88	3.87	1.98	2.19	
MgO	1.28	1.94	.22	.30	tr.
CaO	3.04	2.37	.88	.96	.7
Na_2O	4.34	4.62	3.19	3.84	2.7
K_2O	3.18	3.12	5.55	5.11	5.7
H_2O+	.74	1.04	.77	.54	
H_2O-	.11	.07	.05	.09	
TiO_2	.48	.46	.34	.41	.15
P_2O_5	.16	.29	.06	.06	.02
MnO	.08	.12	.06	.10	.06
ZrO_2					
F	.07		.10	.08	
CO_2					
S					tr.
BaO					
Cr_2O_3					
NiO					
Less O for F or S	-.03		-.04	-.03	
TOTAL	99.97%	99.70%	99.35%	99.74%	99.73%

Sample No.	(72)	(73)
SiO_2	72.0 %	75.0 %
Al_2O_3	13.0	11.7
Fe_2O_3	5.0	3.9
FeO		
MgO	.1	tr.
CaO	.6	.6
Na_2O	3.5	3.7
K_2O	5.4	4.2
H_2O+		
H_2O-		
TiO_2	.20	.18
P_2O_5	.04	.09
MnO	.08	.06
ZrO_2		
F		
CO_2		
S	tr.	.01
BaO		
Cr_2O_3		
NiO		
Less O for F or S		
TOTAL	99.92%	99.44%

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VITA

Eva Bognar Kisvarsanyi was born in Budapest, Hungary, on December 18, 1935. Her father is a meteorologist, her mother works as a secretary. She has one younger brother who attends high school.

She attended the Varga Katalin High School in Budapest from 1950 until 1954. In 1954 she entered the Eotvos Lorand University of Budapest where she studied geology. In 1956 she was married to Geza Kisvarsanyi, chief geologist at the Hungarian Geological Survey, formerly an assistant professor at the Eotvos Lorand University.

The Hungarian revolution in October, 1956, interrupted her studies. In December, 1956 she and her husband left their country and came to the United States to start a new life here.

In March, 1957, she enrolled at the Missouri School of Mines and Metallurgy, graduated with First Honors in May, 1958, with the Bachelor of Science degree in Geology.

During the following fall semester she did field work for her thesis in Southeastern Missouri with financial assistance from the Missouri Geological Survey. The thesis is in partial fulfillment for the Master of Science degree, Geology major.